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VOC reactivity and its effect on ozone production during the HaChi summer campaign

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Abstract. Measurements of ozone and its precursors conducted within the HaChi (Haze in China) project in summer 2009 were analyzed to characterize volatile organic compounds (VOCs) and their effects on ozone photochemical production at a suburban site in the North China Plain (NCP). Ozone episodes, during which running 8-h average ozone concentrations exceeding 80 ppbv lasted for more than 4 h, occurred on about two thirds of the observational days during the 5-week field campaign. This suggests continuous ozone exposure risks in this region in the summer. Average concentrations of nitrogen oxides (NO_x) and VOCs are about 20 ppbv and 650 ppbC, respectively. On average, total VOC reactivity is dominated by anthropogenic VOCs. The contribution of biogenic VOCs to total ozone-forming potential, however, is also considerable in the daytime. Key species associated with ozone photochemical production are 2-butenes (18 %), isoprene (15 %), trimethylbenzenes (11 %), xylenes (8.5 %), 3-methylhexane (6 %), n-hexane (5 %) and toluene (4.5 %). Formation of ozone is found to be NO_x-limited as indicated by measured VOCs/NO_x ratios and further confirmed by a sensitivity study using a photochemical box model NCAR_MM. The Model simulation suggests that ozone production is also sensitive to changes in VOC reactivity under the NO_x-limited regime, although this sensitivity depends strongly on how much NO_x is present.

1 Introduction

The key role of VOCs in fueling photochemical processes was first identified by Haagen-Smit (1952). Since then it has been well recognized that chemical processes involving VOCs and NO_x lead to the generation of ozone and other secondary pollutants in the presence of sunlight (Seinfeld, 1989; Seinfeld and Pandis, 1998; Sillman, 1999). Photochemically produced ozone has received considerable attention in virtue of its potential adverse effects on public health and agricultural productivity when exceeding ambient standards (USEPA, 2006). As a consequence, great efforts have been undertaken in the past decades to address the problem of high ozone concentrations and to advance understanding of the processes controlling ozone formation (Committee on tropospheric ozone formation and measurement, 1991; Chameides et al., 1992; Kleinman, 2000, 2002; Steiner et al., 2008; Geng et al., 2008; Ran et al., 2009). In particular, it is critical to unravel ozone precursor relationships and to evaluate the relative importance of various VOCs in ozone production for the purpose of developing effective control measures.

The magnitude and composition of the overall VOC mixture in the ambient atmosphere depend on emissions, chemical transformation, transport and deposition. A number of papers on VOCs have covered different aspects including chemical mechanisms (Atkinson, 1990, 2000; Dodge, 2000), measurement techniques (Kelly and Holdren, 1995; Wang et al., 2004; Chang et al., 2010), reactivity scales (Darnall et al., 1976; Carter et al., 1994; Dimitriades, 1996; Derwent et al., 1998) and emission inventories (Guenther et al., 2000;

Liu et al., 2008; Tsui et al., 2009). Recently, VOC oxidation leading to formation of secondary organic aerosols (SOA) has also been of interest (Claeys et al., 2004; Volkamer et al., 2006). However, due to the high diversity of VOC groups, the wide range of VOC reactivities, the spatial and temporal variability of VOC sources and the lack of emission inventories, it is not surprising to find difficulties in quantifying total VOCs, identifying a variety of emission sources and assessing ozone-forming potentials for individual species. Knowledge regarding VOCs is still rather limited and specific explorations of VOC properties and their effects on ozone formation in different locations are required.

China has experienced rapid economic growth in the past decades. Many cities have been through fast expansion involving population explosion, overloaded traffic, increasing industrial facilities and anthropogenic activities. The emergence and development of megacities and city clusters lead to widespread and profound influences on air quality, not only limited to those cities themselves, but also on a regional scale (Molina and Molina, 2004; Lawrence et al., 2006; Zhang et al., 2007). The North China Plain (NCP), in which a cluster of densely populated cities including two megacities Beijing and Tianjin are located, is one of the most polluted regions in China (Shao et al., 2006). A substantial degradation of air quality, such as haze and ozone pollution, has arisen from rapid urbanization and industrialization in this region. Concerns have been raised about the ozone pollution problem in the NCP, where numerous anthropogenic sources of ozone precursors exist in addition to biogenic sources (Wang et al., 2006; Lin et al., 2008; Duan et al., 2008; Wang et al., 2009; Lu et al., 2011). Most of previous studies in the NCP focused on ozone photochemical processes at rural sites or in urban Beijing. At a regional background site Shangdianzi, the transition between NO_x-limited and NO_x-saturated photochemistry was indicated (Ge et al., 2010). In urban Beijing, ozone production was often found to be VOC-sensitive (e.g., Shao et al., 2009; Tang et al., 2010). Wang et al. (2006) observed ozone enhancement in urban plumes at a downwind rural site north of Beijing and reported strong correlations between ozone and NO_y. However, it was for the first time that ozone photochemistry was investigated at a suburban site, which lies in between a cluster of urban centers in the polluted NCP, especially the twin megacities Beijing and Tianjin. As a starting point, the extensive filed campaign conducted in summer 2009 would help improve understanding of ozone photochemistry in this region and provide an insight into the development of ozone control strategies on a regional scale. Here we present analyses of observational data collected during the HaChi summer campaign. General information on the experimental data is given in Sect. 2. The characteristics of ozone and its precursors are presented in Sect. 3.1, followed by discussions on potential VOC sources in 3.2 and ozone photochemical sensitivity in 3.3. Finally is a summary of conclusions.
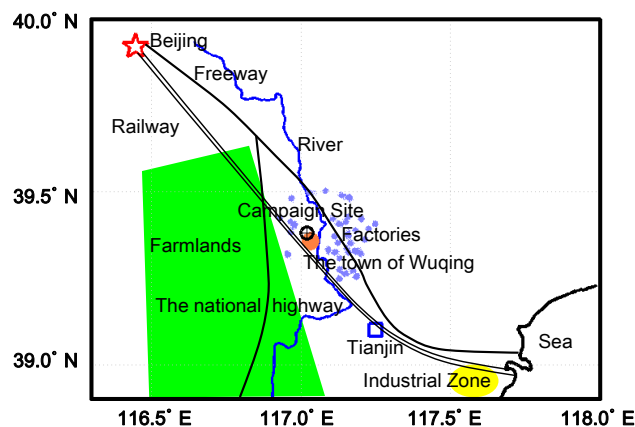

Fig. 1. A sketch of the campaign site and its surroundings.

2 Experiment

2.1 Site description

The HaChi summer campaign was carried out between 10 July and 13 August, 2009 in Wuqing, Tianjin. Figure 1 is a sketch of the site and its surroundings. Measurements of ozone and its precursors VOCs and NO_x were conducted at the Wuqing meteorological station (39° 23′ N, 117° 01′ E, 7.4 m a.s.l.) northwest of the Wuqing town, which is nearly 80 km to the southeast of the megacity Beijing and 30 km to the northwest of the megacity Tianjin. The campaign site is surrounded by a number of small factories within a distance of 10 km. Most of the neighboring industrial sources are clustered to the east of the site, including paper mills, refrigerator plants, furniture and paint manufacturing factories, organic chemical reagent producers, leather manufactures, power plants, food manufactures and metal surface processing factories. Moreover, an active petrochemical complex is situated in the heavily industrialized zone near the coastal area. To the west and south of Wuqing, the landscape is generally agricultural-oriented in land use and land cover, with railways and busy roads running through.

2.2 Measurements

During the campaign, ground level ozone and NO_x were continuously monitored using instruments from Thermo Environmental Instruments (USA), together with meteorological parameters observed by Automatic Weather Station installed at the site. Multipoint calibrations and daily maintenance were operated according to USEPA recommendations on quality assurance and quality control (USEPA, 2008). Measured ambient concentrations were reported as one-min average mixing ratios by volume (ppbv). More details of the instrumentation for reactive gases are described in Xu et al. (2011). In particular, it should be noted that NO_x measurements with a molybdenum converter as was in our

Table 1. Daily averaged chemical parameters for six cases in the NCAR_MM model.

Case/ppbC	Day	Total Propy-Equiv Concentration	Alkanes	Alkenes	Aromatics	Oxygenates
1	Aug. 7	140	30 (22 %)	23 (17 %)	78 (56 %)	8 (5 %)
2	Aug. 8	160	48 (31 %)	29 (18 %)	72 (45 %)	10 (6 %)
3	Aug. 9	175	58 (33 %)	35 (20 %)	74 (42 %)	9 (5 %)
4	Aug. 10	182	37 (20 %)	57 (31 %)	81 (45 %)	7 (4 %)
5	Aug. 11	237	41 (17 %)	112 (48 %)	79 (33 %)	5 (2 %)
6	Aug. 12	205	40 (20 %)	78 (38 %)	82 (40 %)	5 (2 %)

field campaign would lead to an overestimation, especially in nonurban areas where reactive nitrogen compounds such as HNO_3 and PAN formed during the course of transport from urban areas would be partly converted to NO and taken as a part of NO_x (Parrish and Fehsenfeld, 2000; Steinbacher et al., 2007). Therefore, measured NO_x is an upper limit of the real NO_x level in the ambient atmosphere. In the following sections, NO_x is denoted by NO_x* when measured concentrations are described, otherwise remains NO_x.

Sampling of VOCs was conducted for a week with a sampling protocol designed to capture the diurnal variation profile. Five periods (07:30–09:30 a.m., 11:00–13:00 a.m., 14:00–16:00 p.m., 17:00–19:00 p.m. and 21:00–23:00 p.m.) were selected on each day for sample collection from evening 6 August to midday 13 August. An 8L Teflon bag was used to collect the ambient air at a 30-min interval during each sampling period. Thus, each VOC sample represented an average condition of the 2-h sampling period. Subsequent analysis was carried out in the laboratory following USEPA methods TO-14A and TO-15 (USEPA, 1999a, 1999b). Air samples were analyzed using a GC/MS system, which is composed of a gas chromatograph (Agilent GC7890) equipped with a mass-selective detector (Agilent MSD5975C). A total of 102 VOC species were identified and quantified, including 28 alkanes, 10 alkenes, 17 aromatics, 10 oxygenates and 37 halogenated hydrocarbons.

2.3 Data analysis

Statistical analysis of ozone and NO_x is based on a dataset with data completeness greater than 75 percent on each of the 30 days during the 5-week campaign. Consequently, the dataset should have good representativeness of the characteristics of photochemical pollutants in the summer. Average concentrations of ozone and NO_x are calculated for each hour, in which more than 75 % of the data are valid. Running 8-h average ozone concentration is computed from hourly data for each hour and the result is stored in the first hour (USEPA, 1998). VOC species are expressed as ppbv, ppbC and Propy-Equiv ppbC. The Propy-Equiv concentration is obtained by utilizing one of the OH-reactivity

weighted methods following Chameides et al. (1992),

$$Propy-Equiv(J)=C_J \frac{k_{OH}(J)}{k_{OH}(C_3H_6)}$$

Where C_J is the quantified ppbC concentration of species J, k_{OH} is the reaction rate of individual VOC species with OH radical (obtained primarily from Atkinson, 1990, also from Middleton et al., 1990 and DeMore et al., 1997).

2.4 Observation based modelling approach

To determine ozone precursor relationships and the relative importance of various VOC species in ozone formation, a zero dimensional photochemical box model (NCAR Master Mechanism) was used for this study based on in situ measurements of ozone precursors. The NCAR-MM model consists of nearly 5000 reactions with detailed gas phase chemical mechanisms, which simulates how an initial air parcel chemically evolves with time (Madronich and Calvert, 1990; Herring et al., 1997). Model simulations could be performed with user defined input parameters, such as constrained species concentrations, temperature, dilution and boundary layer height. A Tropospheric Ultraviolet and Visible Radiation (TUV) model (Madronich and Flocke, 1998) is coupled into the NCAR-MM model to calculate the photolysis rates needed for photolytic reactions. Different simulation environment could be selected by user specified inputs such as location, time, elevation, and optical depth of cloud and aerosols.

Six cases were arranged according to major components of measured VOCs during each five sampling periods on each day of 7–12 August (daily averaged parameters listed in Table 1). NO_x was maintained constant with adjusted NO_2 concentrations. The concentrations of constrained NO_x were switched in turn from 5, 10, 15, 20, 30, 40 to 60 ppbv for each case, which led to 42 model runs in total. A 5-day model run was conducted and the results on the last day after arriving at a stable state were employed. In each model run, concentrations of constrained species were always reset to prescribed values and repeated on each day, while concentrations of unconstrained species were allowed to accumulate until stabilized. In order to leave out possible influences of meteorological factors on ozone production and help ensure
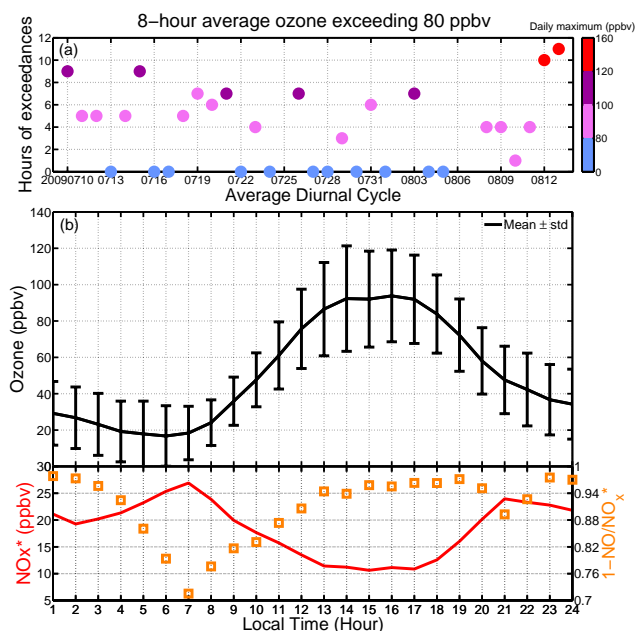
Fig. 2. (a) The number of hours in which running 8-h average ozone concentrations exceeding 80 ppbv on each day. Color bar gives the daily maximum 8-h average ozone concentrations; **(b)** Average diurnal cycle of ozone and NO_x* during the campaign based on 1-h averages.

Fig. 3. (a) The time series of total VOCs expressed as ppbC and Propy-Equiv ppbC, respectively; **(b)** Averaged VOC composition for five sampling periods based on ppbC and k_{OH} scales.

that only photochemistry was responsible for different ozone behaviors in the model simulations, input settings other than chemical parameters were set to be the same among all cases. The boundary layer height was fixed to 1 km, as well as the ambient temperature with 298 K. Photolysis rates were calculated based on the same parameters in the given location.

3 Results and discussion

3.1 Diurnal variations of ozone and its precursors

Ozone episode, defined as daily maximum 8-h average ozone concentration exceeding 80 ppbv, was frequently encountered during the campaign (Fig. 2a). On about two thirds of the observational days, the occurrence of running 8-h averages in excess of 80 ppbv was found to last for more than 4 h, sometimes even as long as 10 h, implying high ozone exposure risks for vegetations and outdoor human activities at Wuqing in the summer. Inspection of average ozone diurnal profile in terms of hourly data could also tell a potential health risk resulting from persisting high ozone in the daytime (Fig. 2b). Daily maximum 1-h ozone concentrations averaged about 90 ppbv with the highest reaching nearly 200 ppbv. During the 5-week campaign, daily maximum 1-h ozone concentration was found to exceed 100 ppbv on 12 days and 120 ppbv on 5 days.
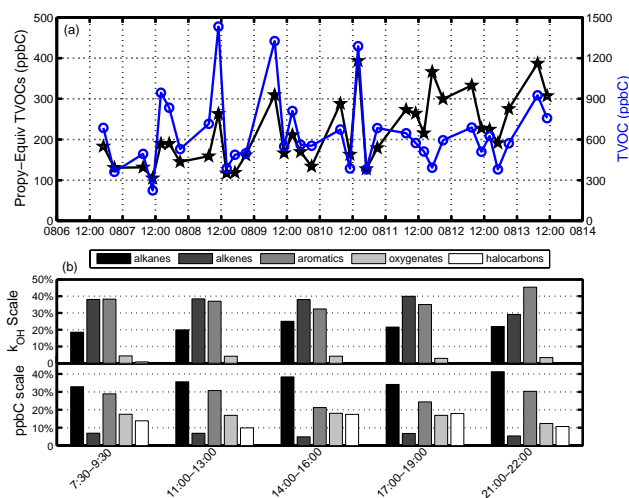
Figure 2b displays the average diurnal cycles of ozone and NO_x* during the campaign using hourly data. Measured ozone concentrations averaged 30 ppbv at night, which is probably attributed to insufficient NO titration process due to limited local NO emissions. However, there were occasional exceptions when nighttime ozone was almost completely consumed. Before early morning, ozone concentrations gradually decrease, mainly as a result of depletion by freshly emitted NO when the development of planetary boundary layer favors accumulations of primary gas pollutants. The concentration of NO_x* is the highest in the morning where the ratio of (NO_x*-NO) to NO_x* is the lowest. On average, NO_x* exhibits a double-peak diurnal pattern, with a daily average of 20 ppbv and a minimum level of about 10 ppbv in the afternoon. Major NO_x sources in Wuqing include power plants, industrial processes and transportation. The buildup of ozone is quite efficient before reaching a daily maximum in the afternoon, with an average accumulation rate of 10 ppbv per hour. Accordingly, the daytime conversion of NO to NO_2 is also quite efficient. After sunset, ozone photochemical production terminates as commonly recognized. Surface ozone goes down slowly with tens of ppbv to be carried over night. On several days, nighttime ozone was observed to be as high as about 70 ppbv. For those particular cases, the high concentrations of ozone might be ascribed to regional mixing over the polluted NCP that brings in ozone-rich air, in addition to insufficient titration that could not completely consume ozone produced photochemically in the daytime.

In contrast to ozone and NO_x, a general diurnal pattern is not found in collected VOCs as illustrated in Fig. 3a. Total VOC concentrations range from 50 ppbv to 425 ppbv and average about 170 ppbv (not shown in Fig. 3). For carbon

atom based mixing ratios, the average concentration of to-tal VOCs is about 650 ppbC within a range of 220 ppbC and 1400 ppbC. Propy-Equiv concentrations that count in differences of individual species in OH-reactivity vary between 100 ppbC and 390 ppbC with an average of 220 ppbC. It should be noted that the time series of total VOCs in Fig. 3a reveals a discrepancy when examined by carbon atom mixing ratios and reactivity weighted concentrations, presumably implying pronounced changes in the composition of the overall mixture. Therefore, we should bear in mind that the characteristics of VOC composition and reactivity, derived from an averaged dataset and described below in the remaining part of Sect. 3.1, only represent an average condition of VOC properties through the entire sampling period and are subject to further investigations to avoid a misleading view given by the averages. Related analysis and discussions are furthered in Sect. 3.2.

Averaged VOC composition depicted in Fig. 3b is obtained with carbon atom mixing ratios as well as OH-reactivity weighted concentrations for the five sampling periods selected on each day. For the carbon atom mixing ratio metric, about 30 % of the measured VOCs are made up of alkanes, which are mainly comprised of species with more than five carbon atoms. Aromatics have a relatively smaller fraction of 25 % compared to alkanes. Alkenes only account for 5 % of total VOCs. The fractions of oxygenates and halogenated VOCs are less than 20 %. However, halogenated VOCs are found to be most abundant when expressed as volume mixing ratios, accounting for roughly 40 % of the overall mixture. The consideration of carbon atoms obviously masks the importance of detected oxygenates and halogenated VOCs in constituting the total mixture, since they are primarily low carbon atom species. Assessed by OH-reactivity weighted concentrations, aromatics and alkenes are of equivalent importance, with an average fraction of nearly 40 %, in their contributions to total VOC reactivity. The highest ranking species with respect to ozone-forming potentials are 2-butenes (10 % for trans-2-butene and 8 % for cis-2-butene), isoprene (15 %), trimethylbenzenes (4 % for 1,3,5-trimethylbenzene and 1,2,4-trimethylbenzene respectively and 3 % for 1,2,3-trimethylbenzene), xylenes (4.5 % for m-xylene, 2.5 % for p-xylene and 1.5 % for o-xylene), 3-methylhexane (6 %), n-hexane (5 %) and toluene(4.5 %). They make up almost 70 % of the total reactivity of all detected species. Isoprene, known to be primarily emitted by vegetation with emission rates dependent on factors such as temperature and light (Guenther et al., 1991, 1993), is of significant importance in fostering episodes of high ozone in Wuqing around the midday. During the daytime, the contribution of isoprene to total reactivity ranges from 10 % to 40 % and averages about 20 %.
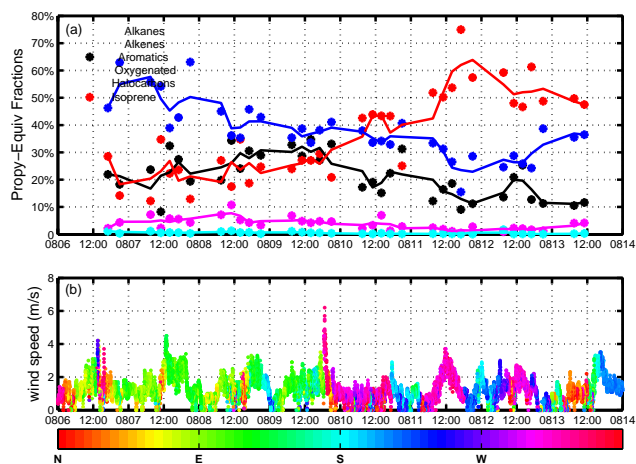

Fig. 4. (a) The time series of VOC composition obtained from the OH-reactivity weighted method. Markers represent the Propy-Equiv fractions for each sampling period of time. Lines represent running averages of 7 samples; **(b)** The time series of surface wind speed and direction (observed at 10 m height) with a temporal resolution of one minute.

3.2 Potential VOC sources

To adequately understand VOC properties observed in the ambient atmosphere and to effectively implement emission controls of various VOCs that play a critical role in ozone photochemical production, source apportionment has long been of particular concern. Moreover, some VOC species are hazardous air pollutants (HAP) according to the USEPA (2002) and necessarily require regulatory controls for emission reductions. Unfortunately, the deficiency of available VOC emission inventories often makes analysis pertinent to VOC source apportionment a tough task. There is, nevertheless, a feasible way to qualitatively analyze potential VOC source types by examining the VOC composition under specific meteorological conditions. When air masses carrying species released from emission sources in different areas pass over the sampling location, it is very plausible that a difference in the number of species or in the concentration level for certain species could be expected, in despite of the influences of chemical transformation and deposition processes.

When the first VOC sample was collected in the evening of 6 August, typhoon "Morakot" just commenced to impose its influences on East China. Although the NCP was almost 1000 km far away, the influence of the typhoon on the West Pacific High still led to indirect impacts on meteorological conditions in the NCP. Prevailing easterly winds lasted for almost three days in Wuqing until late 9 August (Fig. 4b), as is consistent with the large scale wind fields. In the evening of 9 August, surface winds turned northwesterly with an instantaneous wind speed of $6 \, \mathrm{m \, s^{-1}}$. After a very short period, local winds gradually decreased to less than $2 \, \mathrm{m \, s^{-1}}$

and continued on throughout the next day. In the following two days, northwesterly winds prevailed in the daytime, while southwesterly winds prevailed at night. Accordingly, it is interesting to notice that the major components of total VOC reactivity, aromatics, alkanes and alkenes, seem to experience different changes in their relative importance to total reactivity before and after 10 August (Fig. 4a). The sampling period could be subdivided into two periods either depending upon VOC composition in terms of Propy-Equiv fractions or surface winds. Thus, the changes of meteorological conditions during the sampling period as indicated above probably provide a good chance to analyze potential VOC sources in Wuqing.

Period 1, from 7 August to the afternoon of 9 August, continuously experienced the passage of air parcels from industries and urban cores to the east of the sampling site. The prevailing easterly winds that persisted for days made it possible for VOC species to be even long-range transported from the petrochemical facilities near the coastal area. During period 1, average concentrations of total VOCs were 700 ppbC and 180 Propy-Equiv ppbC, respectively. Aromatics made a contribution of 40 % to the total reactivity with an average Propy-Equiv concentration of 72 ppbC. Averaged Propy-Equiv concentrations of alkenes and alkanes were about 40 ppbC and 50 ppbC, respectively. Ozone and NO_x^* data on 7 August and in the morning of 8 August were unfortunately unavailable due to a power failure. For the rest of Period 1, NO_x^* concentrations averaged around 19 ppbv. Daily maximum 1-h ozone concentrations were 97 ppbv and 104 ppbv for each day.

Period 2, from 11 August to 12 August, is thought to be mainly affected by vegetative emissions in the western and southern areas of the NCP. During period 2, the OH-reactivity of alkenes increased dramatically to about 150 ppbC and composed 56 % of the total reactivity. The reactivity of alkanes slightly declined to 40 Propy-Equiv ppbC in period 2. It is found that the Propy-Equiv concentrations of aromatics actually remained relatively stable throughout the whole sampling period. Therefore, the difference in total reactivity and composition between the two periods was largely due to the increase of alkene concentrations. Total VOC mixture was mainly composed of reactive alkene species in period 2 and had a corresponding higher ratio of Propy-Equiv concentration to carbon atom based concentration as 0.47, compared to a value of 0.25 in period 1. NO_x^* increased slightly from 19 ppbv in period 1 to 22 ppbv in period 2. For ozone, episodes of high concentrations continued in period 2 with an elevated daily peak up to 140 ppbv. 10 August is considered to be a transition between the two periods and not included in either period to eliminate the influences of VOC features in period 1 on that in period 2.

The average concentration of individual VOC species is calculated for each period, in order to gain a further insight into potential VOC sources contributing to the measured VOC mixture in the sampling location. Detailed analysis is discussed in view of three categories as shown in Fig. 5. The first category involves species with concentrations averaged over period 2 higher than the double of concentrations averaged over period 1, whereas species of reversed situation are grouped into the second category. The third category contains all those species not in category 1 and 2, except for 21 species that were detected neither in period 1 nor in period 2. Species in the third category have comparable concentrations for both periods.

Alkenes are almost exclusively classified to the first category. Propene and 1-butene could be either of biogenic origin or of anthropogenic origin such as automobiles and chemical industries (Kesselmeier and Staudt, 1999; USEPA, 2002). It is presently difficult to tell how much of the observed concentrations should be assigned to each source type. Species like 2-butenes, pentene, propane, butanes and methylpentanes could be released into the atmosphere by vehicular exhaust, the evaporation of gasoline and industrial processes. The traffic burden on the national highway in the west is heavier compared to roads in any other direction, presumably contributing to a higher level of those species in period 2.

As for isoprene, it has been known to be mainly released by vegetation. Nevertheless, isoprene could also be of anthropogenic origin. The traffic emission of isoprene has been reported at both urban and rural locations (e.g., McLaren et al., 1996; Reimann et al., 2000; Borbon et al., 2001). Besides, isoprene is largely used in the manufacture of synthetic rubber. During the sampling period, isoprene was found to be poorly related to methyl tert-butyl ether (MTBE) as indicated in Fig. 6b and c. MTBE is a comprehensive additive in fuels in China and unlikely to be found in any other sources. It serves as a reliable tracer for vehicular emissions (Chang et al., 2003). The poor correlation between isoprene and MTBE thereby indicates that the traffic origin of isoprene is negligible in this region. In addition, the temporal variation of isoprene was almost opposite to that of vinyl chloride, an indicator of petrochemical industries (Na et al., 2001). Actually, vinyl chloride was hardly detected during period 2 when very high concentrations of isoprene were observed. Hence, the petrochemical origin of isoprene would be rather minor if not completely impossible. Figure 6a shows the time series of isoprene. An increase in isoprene concentrations from less than 2 ppbv during period 1 to nearly 14 ppbv during period 2 is supportive of its biogenic origin in the western and southern vegetated areas. Enhanced vegetative emissions of isoprene in response to a five degree increase in temperature during period 2 from 30° during period 1 would also be partially responsible for observed higher isoprene concentrations during period 2. It is noteworthy that the diurnal profile of isoprene in period 2 is quite different from the normally well defined diurnal pattern. Since emission rates of isoprene are determined by leaf temperature and light intensity according to Guenther et al. (1991, 1993), the highest isoprene concentrations are often found in the afternoon when biogenic emissions tend to
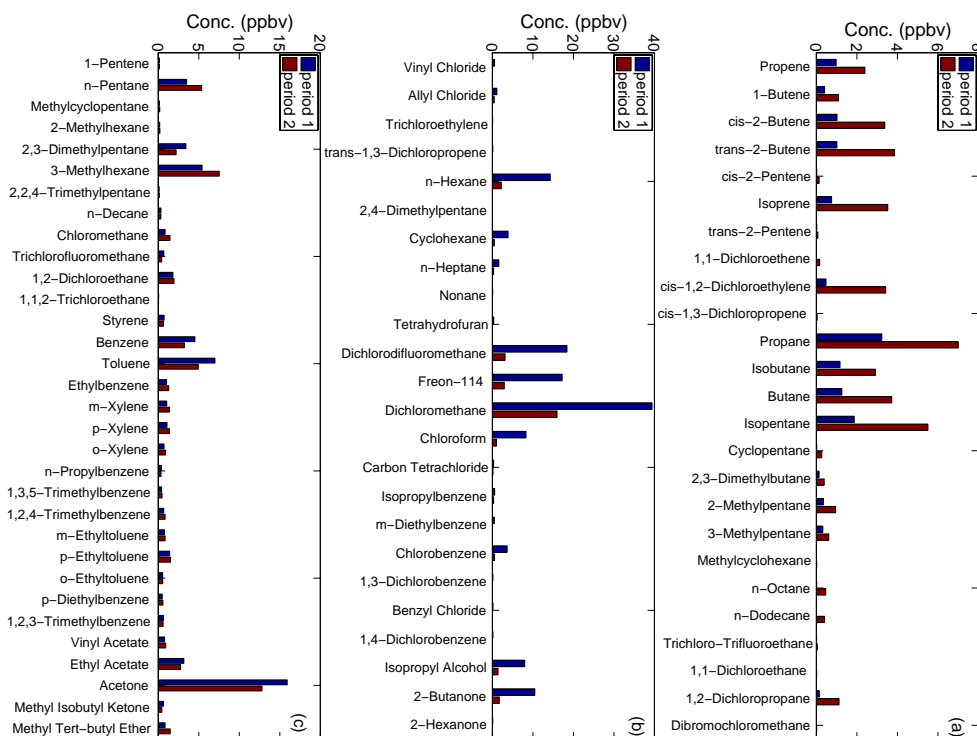
Fig. 5. Concentrations averaged over period 1 (denoted by C1) and period 2 (denoted by C2) for individual VOC species, except for 21 species that were not detected in both periods: **(a)** the first category: C2 > 2*C1; **(b)** the second category: C1 > 2*C2; **(c)** the third category: all those species not in category 1 and 2, whose average concentrations of both periods are comparable.
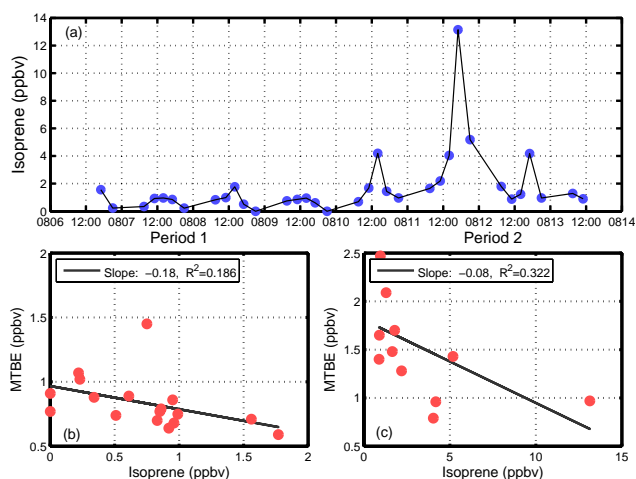

Fig. 6. (a) The time series of isoprene during the sampling period; **(b)** Plots of correlations between isoprene and MTBE during period 1; **(c)** Plots of correlations between isoprene and MTBE during period 2.

be the strongest. Interestingly, isoprene peak was delayed to late evening (as observed in period 2) instead of appearing in the afternoon (as observed in period 1) in our field study. Usually, isoprene reacts quickly with OH radicals after emit-

ted into the atmosphere and has consequently a very short lifetime. However, it is likely that the huge amount of isoprene emitted in the passage of transport has consumed available OH radicals, thus helps reshape observed diurnal cycle and maintain a high level even late into the night. To support this hypothesis, further efforts involving the development of VOC emission inventories, and direct measurements of free radicals and major isoprene degradation products along the transport pathway would be highly appreciated.

VOCs that fall into the second category include halogenated species and hydrocarbons mainly associated with industrial emissions. Hexane, currently used in many industrial fields such as furniture, food and leather manufacturing processes, is a HAP (USEPA, 2002) and detrimental to human nervous system. Hexane is the most abundant species measured in Wuqing expressed as ppbC. It could be clearly seen in Fig. 5 that the average concentration of hexane during period 1 was 15 ppbv, approximately 6 times of that during period 2, suggesting factories to the east of the sampling location to be its major sources. Isopropyl alcohol is another widely used industrial material. As an important solvent in paper making, the evaporation of isopropyl alcohol contributes largely to the measured concentration at the site. Possible sources for a high level of halogenated hydrocarbons detected in the overall mixture are industrial and residential refrigerants, also evaporation of solvents in chemical

industries. As mentioned above, vinyl chloride, a tracer for petrochemical emissions (Na et al., 2001), is only detected in period 1 and could serve as a fingerprint of heavily polluted air masses from the coastal industrial area.

The major components in the third category are aromatics that often share a variety of sources, including solvent usage, traffic and industries. Despite different meteorological conditions in the two periods, the average concentrations of most aromatics remained close to each other. Moreover, aromatic species including toluene, xylenes and trimethylbenzenes that are most important to ozone photochemical production have undergone a similar diurnal variation day by day. This suggests the existence of relatively stable sources like local traffic emissions and industrial activities for those species either on local or regional scales. The traffic emission indicator MTBE averaged about 1 ppbv throughout the sampling period, with a slightly higher level in period 2 to be reasonably explained by aforementioned traffic loadings around the campaign site.

3.3 Ozone photochemical sensitivity

Ozone photochemical sensitivity could be determined by an empirical approach of examining the ratios of measured ambient VOCs (ppbC) and NO_x^* (ppbv). All of the VOCs/ NO_x^* ratios are found to be larger than 10. The average diurnal variation of VOCs/ NO_x^* ratios gives a value of about 30 in the morning. This ratio increases dramatically to about 70 during the daytime, falls in the evening to the same level as in the morning and stays the lowest at night with a value of about 22. Since not all VOC species are able to be quantified by current sampling and analytic techniques, there is an underestimate in total VOC concentration. On the other hand, measured NO_x is overestimated due to interferences of NO_x oxidation products as indicated in Sect. 2.2. Thus, the actual VOCs/NO_x ratios could be even higher and definitely indicate NO_x-limitation of ozone photochemistry. This ozone precursor relationship implies that even a slight increase in NO emissions might lead to dramatic ozone enhancement. Therefore, downwind urban areas could suffer from severe ozone pollution when plumes pass by carrying the highly reactive VOC mixture and encounter high NO_x concentrations in those urban centers. A sensitivity study is further performed by a photochemical box model NCAR-MM through a set of observation-based cases as described in Sect. 2.4. Simulation results are shown in Fig. 7. The behavior of ozone in response to varied NO_x is basically the same for each case. In general, ozone daily maximum increases with increasing NO_x before NO_x reaches a certain concentration, which varies in the range of 20 to more than 30 ppbv according to different VOC reactivity and composition in each case, thereafter turns to be declining with increasing NO_x. The NO_x level above which ozone sensitivity shifts from NO_x-limitation to VOC-limitation, not surprisingly, is higher in cases that involve more reactive species
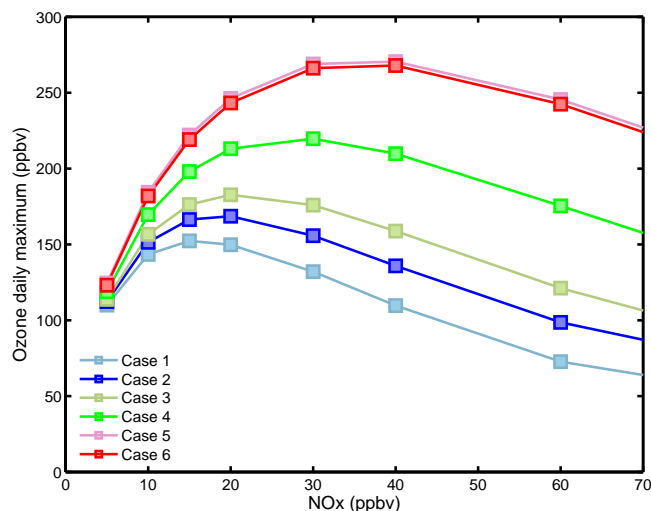

Fig. 7. NCAR-MM model simulation results. Six cases are based on measurements of VOCs on each day of 7–12 August, with all other parameters set to be the same. The square markers are selected cases for $NO_x = 5, 10, 15, 20, 30, 40$ and 60 ppbv.

than in those with lower VOC reactivity. The transition chemical regime should correspond to a higher NO_x concentration, considering an underestimate of the overall VOC reactivity in the model, where only a subset of speciated VOCs are capable of being specified as model inputs. Furthermore, differences in modeled secondary VOCs and actual VOC oxidation products in the atmosphere might either amplify or mitigate aforementioned transition shift to some extent, making it somewhat complicated to clearly distinguish the maximum ozone production regime. Nevertheless, NO_x-limitation could still be confirmed given current VOCs and NO_x levels in Wuqing, where an upper limit of daytime NO_x averages about 10 ppbv. Model simulations also suggest that ozone production is sensitive to changes in VOC reactivity under the NO_x-sensitive regime, although this sensitivity depends strongly on how much NO_x is present. As a consequence, an increase in reactive VOC species like biogenic VOCs, that takes place under favorable meteorological conditions and significantly raise total VOC reactivity as described above, might aggravate local ozone problem and make it even worse when accompanied by increased NO_x. Therefore, the efficacy of strategies designed to reduce ozone would require the control of VOCs in addition to NO_x controls, especially of those photochemically reactive VOC species.

4 Conclusions

A 5-week field campaign was conducted in summer 2009 at a suburban site, which lies in between the twin megacities of Beijing and Tianjin in the polluted NCP and representative

of the regional condition. Observation-based analyses have been performed to investigate the characteristics of VOCs and ozone precursor relationships in this densely populated region with active industries.

Ozone episodes were frequently encountered during the field campaign. On two thirds of the observational days, more than four hours were continuously observed with running 8-h average ozone concentrations above 80 ppbv, suggesting that ozone exposure risks could persist for hours even until late evening in the summer. Generally, ozone was quickly generated after the sunrise and reached the daily maximum in the afternoon with an accumulation rate of about 10 ppbv per hour. The highest summertime 1-h ozone concentration was nearly 200 ppbv. At night, ozone concentrations remained averagely 30 ppbv with a high level of about 70 ppbv on several days, which was probably attributed to regional mixing of ozone over the polluted NCP and insufficient NO titration of local ozone generated photochemically in the daytime.

The diurnal variation of measured NO_x* displays a double-peak profile, which is generally governed by anthropogenic emissions and the evolution of planetary boundary layer. VOCs show much more complexity in the variations of concentration and composition, as a result of various emission sources, transport and chemical transformation. Total VOC reactivity is dominated by anthropogenic species, including aromatics, alkanes and most alkenes, which are largely emitted from industrial facilities, motor vehicles and evaporation of solvents. The importance of biogenic VOCs to ozone photochemical production is notable in the daytime, especially under favorable meteorological conditions. The most reactive species responsible for ozone formation are mainly alkenes and aromatics such as 2-butenes (18 %), isoprene (15 %), trimethylbenzenes (11 %), xylenes (8.5 %) and toluene (4.5 %).

Ozone photochemical production is typically limited by NO_x under current precursor conditions. In addition to empirically examining observed VOCs/NO_x* ratios, a box model is employed to determine the sensitivity of ozone formation to changes in NO_x concentration and VOC reactivity. Model results suggest NO_x-limitation of ozone photochemistry, implying ozone enhancement in response to increasing NO emissions. Thus, NO_x controls should be considered over the NCP, where biogenic and industrial emissions of highly reactive VOCs exist on a regional scale and would drastically give rise to high ozone episodes when high NO_x concentrations are encountered. Moreover, formation of ozone is also found to be sensitive to changes in VOC reactivity even in the NO_x-limited regime, although this sensitivity depends strongly on how much NO_x is present. As a result, an increase in reactive VOCs, such as biogenic VOCs, would exacerbate local ozone pollution problem by significantly raising total VOC reactivity. This situation might be even worse when NO_x level is high at the same time, especially in urban areas. Therefore, control strategies of VOC emissions on a regional scale are necessarily required in addition to NO_x controls for the purpose of reducing potential health risks caused by photochemically produced ozone. Since few measures can be undertaken to reduce background biogenic VOCs by controlling regional biogenic emissions, it is more feasible to target controls of anthropogenic emissions. Reliable and detailed VOC emission inventories should be established and would be valuable for designing effective VOC controls by quantitatively assessing contributions of different source types to photochemically reactive VOC species. It should also be noted that the results presented above were derived from 1-week measurements of VOCs during the HaChi summer campaign. Further investigations based on extensive field experiments are needed in the future to obtain more detailed and robust conclusions. Systematic measurements of VOCs with higher temporal resolution, such as using online proton transfer reaction mass spectrometer (PTR-MS), would be useful to better understand the characteristics of VOCs and their effects on ozone photochemical production in this region.

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