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Ozone production in the megacities of Tianjin and Shanghai, China: a comparative study

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ACPD
12, 9161–9194, 2012

Abstract

Rapid economic growth has given rise to a significant increase in ozone precursor emissions in many regions of China, especially in the densely populated North China Plain (NCP) and Yangtze River Delta (YRD). Improved understanding of ozone formation in response to different precursor emissions is imperative to address the highly nonlinear ozone problem and to provide a solid scientific basis for efficient ozone abatement in these regions. A comparative study on ozone photochemical production in summer has thus been carried out in the megacities of Tianjin (NCP) and Shanghai (YRD). Two intensive field campaigns were carried out respectively at an urban and a suburban site of Tianjin, in addition to routine monitoring of trace gases in Shanghai, providing data sets of surface ozone and its precursors including nitrogen oxides (NO_x) and various volatile organic compounds (VOCs). Ozone pollution was found to be more severe in Tianjin than in Shanghai during the summer, either based on the frequency or the duration of high ozone events. Such differences might be attributed to the large amount of highly reactive VOC mixture in the Tianjin region. It is found that industry related species like light alkenes were of particular importance in both urban and suburban Tianjin, while in Shanghai aromatics dominate. In general, the ozone problem in Shanghai is on an urban scale. Stringent control policies on local emissions would help reduce the occurrence of high ozone concentrations. By contrast, ozone pollution in Tianjin is a regional problem. Combined efforts to reduce ozone precursor emissions on a regional scale must be undertaken to bring the ozone problem under control.

1 Introduction

China has experienced recently an acceleration of economic growth and urbanization. Elevated anthropogenic emissions of primary gaseous pollutants have accordingly been noted in the last few decades, along with a continuous increase to be foreseeable in the near future (Streets and Waldhoff, 2000; Klimont et al., 2001). It is therefore not

ACPD
12, 9161–9194, 2012

surprising that air quality degradation has been extensively reported (e.g., Chan and Yao, 2008, and references therein). The North China Plain (NCP) and the Yangtze River Delta (YRD) are two of the most populated and industrialized regions in China and currently suffer from air pollution in many aspects (Shao et al., 2006). The ground-level ozone problem is among the most stubborn environmental issues, given the ubiquitous existence of the precursors NO_x and VOCs that would photochemically generate ozone when accompanied by sunlight, as has been well documented in a set of research articles (e.g., Haagen-Smit, 1952; Haggen-Smit et al., 1953; Seinfeld and Pandis, 1998). Thus, an urgent need is there to tackle with ozone pollution in these regions where precursor emissions significantly rise, to avoid possible risks in public welfare and ecosystems that might be potentially raised by high concentrations of ozone and its precursors (Chameides et al., 1994; Jacobson, 2002).

Previous studies related to ozone issues in the NCP and YRD regions were carried out separately. Most observations and analysis were performed at regional background sites or in the megacity of Beijing in the NCP (e.g., Gao et al., 2005; Lin et al., 2008, 2009, 2011; Tang et al., 2010; Lu et al., 2010; Xu et al., 2011a). In preparation for the 2008 Olympics, relocation of old industrial facilities away from Beijing and other stringent emission restrictions were implemented to mitigate local air pollution. It turned out that the control of secondary pollutants such as ozone was successful to a lesser extent than most primary gases as a result of regional pollution. A considerable contribution was demonstrated to be made by regional sources like those in Tianjin (Streets et al., 2007; Wang et al., 2010). However, current research regarding the ozone problem in Tianjin is rather limited (Han et al., 2011; Ran et al., 2011; Xu et al., 2011b). In the YRD region, the expansion of population and economics centers around the megacity of Shanghai, where ozone issues have been more elaborately addressed but mostly in the thriving downtown area (e.g., Cheung and Wang, 2001; Zhao et al., 2004; Geng et al., 2008; Tang et al., 2008; Ran et al., 2009). In an effort to understand ozone behaviour in responses to enhanced precursor emissions, and to design feasi-

ACPD
12, 9161–9194, 2012

ble and effective emission control strategies, more work needs to be done in these fast developing regions.

In this paper, detailed analysis of ozone related measurements are comparatively carried out in urban and suburban areas of the two megacities Tianjin and Shanghai. This would hopefully cast more light on understanding and handling current ozone problem in the two megacities. Section 2 provides detailed information on measurements in the four locations. The method of calculating the instantaneous photochemical production rate of ozone is also introduced in this section. Observations of ozone and its precursors are analyzed and compared in Sects. 3.1–3.3. The discussion on ozone production rates is performed in Sect. 3.4. Major conclusions are given in the last section.

2 Experiments and methodology

2.1 Sites

Observations of gaseous pollutants were conducted respectively at an urban and a suburban site in the megacities of Tianjin and Shanghai. Sitting on the eastern edge of the polluted NCP, Tianjin is adjacent to the Bohai Bay as illustrated in Fig. 1a. The Tieta site (39°06′ N, 117°10′ E), where the 2010 summer campaign took place, is located in a thickly settled urban district of Tianjin. The largest petrochemical complex in China has recently been built up in the Tianjin Binhai New Area, which is situated about 40 km southeast of urban Tianjin and extends nearly 150 km along the coastal line. Measurements of ozone and its precursors at the suburban site Wuqing (39°23′ N, 117°01′ E) were carried out during the 2009 Haze in China (HaChi) summer campaign. The site is surrounded by a cluster of urban centers in the NCP and about 30 km away from the Tieta site. Large areas of farmlands stretch for hundreds of kilometers to the west of Wuqing, while most of the local factories are clustered in the east. Two routine monitoring stations are located in Shanghai (Fig. 1b). The Xujiahui site (31°12′ N,

ACPD
12, 9161–9194, 2012

121°26′ E) is located in the crowded metropolitan area, where active commercial activities take place every minute. This area is overburdened with a dense population, high traffic loading, as well as numerous tower buildings. Near the coast and almost 50 km south of the urban center is a petrochemical industrial area, wherein the site of Jinshan (30°45′ N, 121°21′ E) is situated. The residential population is sparse there and the land cover is well vegetated.

In support of related discussions, the observational data of surface ozone during July and August 2009 at another three NCP sites are also used. The urban site in the megacity of Beijing is located in the courtyard of China Meteorological Administration (CMA, 39°57′ N, 116°19′ E), which is between the busy 2nd and 3rd ring roads in the northwest area of urban Beijing (Lin et al., 2011). The site CMA is about 110 km northwest of Tianjin (Fig. 1a). Gucheng (GCH, 39°08′ N, 115°40′ E) is a polluted rural site about 110 km southwest of Beijing and 130 km west of Tianjin (Lin et al., 2009). Shangdianzi (SDZ, 40°39′ N, 117°07′ E) is a WMO regional atmosphere background station on the north rim of the NCP region, showing footprints of polluted regional background and clean natural background according to wind direction (Lin et al., 2008).

2.2 Measurements and data processing

Continuous monitoring of ozone and NO_x took place in July–August 2009 at both sites of Shanghai and in suburban Tianjin, while observations were made during July–August 2010 in urban Tianjin. The commercial Thermo Environmental Instrument (TEI Inc., USA) Model 49C, a UV Photometric Analyzer, was used to measure ozone concentrations at both sites of Tianjin, CMA, GCH and SDZ. Surface ozone in Shanghai was observed using the UV Absorption Ozone Analyzer (EC9810B/ECOTECH) based on the same operation principle. As for the measurements of NO_x, TEI 42CTL NO-NO_2-NO_x Analyzer simultaneously determined the ambient concentrations of NO and NO_x at Wuqing, utilizing chemiluminescence techniques and a heated molybdenum NO_2 to NO converter. This instrument was able to accurately measure the amount of nitrogen oxides to a trace level of less than 50 pptv. TEI 42i used at Jinshan site and EC9841B

ACPD
12, 9161–9194, 2012

Oxides of Nitrogen Analyzer (ECOTECH) used in urban areas of Tianjin and Shanghai were operated on the basis of similar techniques as TEI 42CTL and also capable of measuring NO and NO_x at the same time. Besides, carbon monoxide (CO) was measured by TEI 48C CO Analyzer during the same periods of ozone measurements at both sites of Tianjin. Multipoint calibrations and daily maintenance were carefully performed at all sites following USEPA recommendations on quality assurance and quality control (USEPA, 2008). Mixing ratios (ppbv) of ozone, NO_x and CO were acquired at a resolution of one minute. Hourly averages were calculated to meet the requirement of valid data over 75 % in each hour.

VOC sampling protocols differed among the four sites. At Tieta, a 3.2 l canister was used to continuously collect ambient air samples over each 2-h period (07:30–09:30, 10:30–12:30, 13:30–15:30, 16:30–18:30, and 19:30–21:30) from 22 to 28 August 2010. At Wuqing, samplings were conducted during five periods of time (07:30–09:30, 11:00–13:00, 14:00–16:00, 17:00–19:00 and 21:00–23:00) between 6 and 13 August 2009. An 8 l Teflon bag was used to collect air samples at a 30-min interval, representing the average condition for each 2-h sampling period. At both sites of Shanghai, ambient air was continuously sampled into a 6 l canister over each 3-h period from midnight. Thus, eight samples were obtained respectively on each day of 29 July to 6 August at Jinshan and 25 to 31 August at Xujiahui. Nonetheless, analytic methods for determining specific VOC species were generally the same for all air samples. A total of 52 hydrocarbons including 28 alkanes, 8 alkenes and 16 aromatics were identified and quantified (in mixing ratios, ppbv) using a coupled Gas Chromatography/Mass Spectrometry (GC/MS, Agilent Tech.) in the laboratory according to USEPA methods TO-14A and TO-15 (USEPA, 1999a, b). The carbon-atom based concentration (in ppbC) was another straightforward expression for the measurements. To scale the relative reactivity of various hydrocarbons, the propene equivalent concentration (Propy-Equiv, in ppbC) was calculated for each species. As defined in Chameides et al. (1992), the Propy-Equiv concentration was derived by weighting the carbon-atom based concentration of a single species with the corresponding OH reaction rate constant and then being

ACPD
12, 9161–9194, 2012

normalized to that of propene. The reaction rate coefficients of individual species with OH radical were mostly adopted from Atkinson (1990) and also from Middleton et al. (1990). This widely used scaling approach neglected the impacts of subsequent chemical mechanisms on ozone production after initial OH oxidation, yet provided a simple way for direct intercomparisons.

Meteorological parameters such as temperature, wind and precipitation were recorded in a temporal resolution of one minute by the Automatic Weather Station installed at each site. Limited transport and wet deposition of gas pollutants were expected on days with wind speed less than 4 $m\,s^{-1}$ and without precipitation in the daytime. Since winds were usually stronger in the suburbs than in urban areas, it was believed to be reasonable that data with wind speed less than 6 $m\,s^{-1}$ in the two suburbs should also be counted in. Based on such rules, 19 and 14 days were selected at Tieta and Wuqing, respectively. At Xujiahui and Jinshan, the respective numbers were 10 and 11. Photochemical process was supposed to predominantly contribute to observed ozone concentrations on these selected days. This subset of data was used in Sect. 3.3 to analyze diurnal cycles of ozone and its precursors under photochemistry-dominant circumstances.

2.3 Calculation of ozone production rates

Ozone production is an essential term for determining the extent to which in-situ ozone could be ascribed to photochemistry. According to our current knowledge on the chemical mechanism, it is hydroperoxy radical (HO_2) produced from the oxidation of CO and organic peroxy radicals (RO_2) produced from the oxidation of VOCs that oxidize NO into NO_2 and subsequently lead to net production of ozone by NO_2 photodissociation (Seinfeld, 1989; Atkinson, 1990, 2000; Jenkin and Clemitshaw, 2000). The instantaneous production rate of ozone, usually denoted as $P(O_3)$, could thereby be written as,

$$P(O_3)=[NO](k[HO_2]+\sum_i k_i[R_iO_2]) \quad (1)$$

ACPD
12, 9161–9194, 2012

where k is the rate constant for the reaction of NO and HO_2, and k_i is the rate constant for each reaction of NO and R_iO_2 (Trainer et al., 2000). Several methods have been developed to estimate $P(O_3)$ based on measurements and applied to the analysis of ozone photochemical process (Frost et al., 1998, and references therein; Kleinman, 2000).

In this paper, $P(O_3)$ is calculated using the concentrations of model simulated peroxy radicals and measured NO. A photochemical box model with a detailed description of the chemical mechanism is used to estimate the short-lived radical species (Madronich and Calvert, 1990; Herring et al., 1997; Madronich and Flocke, 1998). Model simulations are initialized by available measurements at 2 p.m. local time and run for half an hour for radicals to reach a steady state in the model before losing the initial information. Two types of chemical inputs are arranged for each site. One is to average the midday VOC data over the sampling period and adjust initial NO_x concentrations from 1 ppbv and 2 to 50 ppbv with an interval of 2 ppbv for each simulation. The other is to perform a simulation for each VOC sampling day by inputting midday VOC data and 30-min averages of measured NO_x. In addition, the set of input parameters other than location information are completely the same. Regardless of the reversible pathway for peroxy radicals to react with NO in forming pernitric acid and organic nitrates that would quickly be decomposed back to their reactants at a prescribed temperature of 303 K in model simulations, peroxy radicals mainly react with NO to yield NO_2 in an amount given by the stoichiometric coefficients. At the end of each model run, model simulated HO_2 and RO_2 are obtained and used for $P(O_3)$ calculation in Eq. (1).

3 Results and discussion

3.1 Probability distributions of ozone and NO_x

Ozone probability distributions (5 ppbv per bin) in all locations are illustrated in Fig. 2a. The occurrence of 1-h average ozone concentrations exceeding 80 ppbv is usually as-

ACPD
12, 9161–9194, 2012

sociated with high ozone episodes that pose threats to human health and welfare. The relatively higher probability of hourly ozone averages over 80 ppbv in Tianjin indicates more severe ozone pollution in this region and also a higher ozone exposure risk for the public compared to that in Shanghai during the summer.

A close similarity could be found in ozone probability distributions at both sites of Tianjin, implying well regional mixing over the polluted NCP. However, we should be cautious to conclude so quickly, given the disagreement of the observational periods. Surface ozone measured at CMA, GCH and SDZ in the NCP were then further examined. The probability distributions of surface ozone at the five NCP sites generally resemble each other, especially at GCH, CMA, Wuqing and Tieta, which lie within a cluster of urban centers in the NCP (Fig. 3a). The frequency distributions of ozone daily maximum and ozone episode (1-h average > 80 ppbv) duration are generally similar among sites, also suggesting ozone pollution is a regional problem in the NCP. This is consistent with the existence of a high-ozone belt peaking between Beijing and Tianjin over the NCP demonstrated by Lin et al. (2009) on basis of the regional distribution of ozone tropospheric column amounts. It can be clearly seen that CO probability distributions in urban and suburban Tianjin are basically the same (Fig. 3b), also in support of well regional mixing of gas pollutants in the NCP. Nevertheless, an extended network of monitoring sites should be needed to provide more solid evidence for regional characteristics. In summer, southwesterly winds prevail in Wuqing, especially for winds below 6 $m\,s^{-1}$. This is also the case for urban Tianjin. The highest ozone concentration of 139 ppbv has been observed at Tieta site, with a mean value of 42 ppbv averaged over the entire summertime. Average concentration of ozone is about 45 ppbv in Wuqing, with the highest value reaching 193 ppbv.

In contrast, ozone probability distribution in urban Shanghai is completely different from that in the suburb. Most hourly data (~ 60 %) are concentrated in the range of 0–20 ppbv in the urban center. The frequency of ozone concentrations between 0 and 5 ppbv is up to nearly 22 %, followed by 15 % in the bin of 5–10 ppbv. Since the monitoring site is located in downtown area where numerous tower buildings are, wind

ACPD
12, 9161–9194, 2012

speeds are generally low and disturbed by turbulence due to canopy effects. Ozone concentrations tend to be more subject to the influences of local chemical and physical processes. Strong NO emission from busy traffic may be most likely responsible for such a high frequency of very low ozone level in urban Shanghai. The highest observed ozone concentration is 124 ppbv and the mean value of all data is 21 ppbv. In suburban Shanghai, average ozone concentration is 37 ppbv, with the highest hourly average to be 139 ppbv. Ozone probability distribution peaks at about 20 ppbv, possibly representing a dynamic balance that is most likely encountered in this location between physical-chemical processes that enhance ozone and that deplete ozone.

As a short-lived species, NO_x is often characterized as more representative of local impacts than long-range transport or regional mixing. Generally, NO_2 (NO_x) pollution is more severe in the NCP region than in the YRD as illustrated in Fig. 1. The in-situ observations have provided us with more details on a smaller scale that satellite data may not be able to distinguish. Different features of NO_x probability distributions could be recognized between urban and suburban areas (Fig. 2b). A much greater portion of the hourly data falls into bins with low concentrations in the suburb than in the urban center. Accordingly, the average level of NO_x in the suburb is much lower. Jinshan is the cleanest location when referring to NO_x, since traffic burden is rather light in this area. Additionally, southeasterly winds dominate in the summer and bring in clean air masses from the East China Sea. Influenced by limited source emissions as well as the dilution, observed NO_x concentrations are often below 10 ppbv and hardly exceed 40 ppbv. The average value is about 11 ppbv, close to the concentration corresponding to the highest probability. In Wuqing, average NO_x concentration is about 20 ppbv, below which almost half of the data are. The probability distribution reaches its maximum around 10–15 ppbv with a sharp decline from the peak value toward either direction. It is noteworthy that the frequency for 0–5 ppbv, unlike in Jinshan, is almost zero in Wuqing. Polluted events with NO_x concentrations in excess of 50 ppbv could also be occasionally encountered in this area. As an industrial and residential area near the transport hub inside the polluted NCP, Wuqing is apparently more polluted than Jinshan. In the

ACPD
12, 9161–9194, 2012

urban centers of both megacities, frequencies of hourly NO_x averages distribute similarly below 100 ppbv. The curves display a maximum between 20–25 ppbv and show the main part in the range of 10–40 ppbv.

3.2 Characterization of VOCs

Average carbon-atom based concentrations of total VOCs and each category in all locations are listed in Table 1. A higher level of total hydrocarbons is found in the Tianjin region (300 ~ 400 ppbC), about 2 to 3 times larger than the overall concentration in Shanghai. In both urban centers, automobile emissions undoubtedly make a substantial contribution to the VOC composition. The traffic indicator methyl tert-butyl ether (Chang et al., 2003) is averagely about 14 ppbC in urban Tianjin and 6 ppbC in suburban Tianjin (not shown in this paper),whereas 1.5 and 0.5 ppbC in urban and suburban Shanghai, respectively. The VOC group in urban atmosphere of the two megacities is similarly composed of about 50 % aromatics, followed by alkanes and alkenes. In the two industrialized suburbs, aside from the marked difference in total concentrations, the compositions also differ remarkably. Over 50 % of the measured VOCs are made up of alkanes in Wuqing, with n-hexane alone to contribute 11 %. Evaporation of solvents used in electronics and pharmaceutical industries probably provides abundant sources for heavy alkanes ($C \geq 5$) as well as certain aromatic species like toluene (10 %) and xylenes (7 %). As could be expected in a thinly populated petrochemical base, the predominant component in Jinshan is the aromatic group (amounting to 72 %) that could be largely released from the process of petroleum refining. Toluene is particularly important, accounting for roughly 50 % of the total mixture. As a matter of fact, the carbon-atom based concentrations of toluene are very close (around 50 ppbC) in Jinshan, urban and suburban Tianjin under the influences of petrochemical emissions. The ambient level of toluene in urban Shanghai is only a half of that in other locations.

VOC reactivity is more relevant to ozone formation in comparison with measured mixing ratio. Based on Propy-Equiv concentrations, the highest VOC reactivity is found in Wuqing with a value of about 200 ppbC (Fig. 4). In urban Tianjin, average Propy-

ACPD
12, 9161–9194, 2012

Equiv concentration of total VOCs is about 130 ppbC. VOC reactivities at both sites of Shanghai are less than one quarter of the VOC reactivity in Wuqing and close to each other. The ratio of Propy-Equiv concentration to carbon-atom based concentration could be treated as a simplified indicator for reactivity related composition. Such ratios (Fig. 4) reveal that the VOC group in Wuqing consists of more reactive species. Reactivity compositions in suburban Shanghai and urban Tianjin are similar, leaving the share of reactive species in urban Shanghai to be the lowest.

The variability of a dataset also has useful implications for data interpretation. Figure 4 gives standard deviations of both Propy-Equiv concentrations and the ratios of Propy-Equiv concentration to carbon-atom based concentration. By examining meteorological parameters during the sampling period, a stable weather condition has been found in urban Tianjin. Variations in temperature and pressure were very limited and wind speeds barely exceeded $3\,m\,s^{-1}$, in favour of local pollution and accumulation. Under such conditions, a distinct diurnal cycle posing a low valley in the afternoon repeated day by day for Propy-Equiv concentrations as well as VOC reactivity related compositions. The large variability in Propy-Equiv concentrations is much attributable to this diurnal variation. In Wuqing, as discussed in Ran et al. (2011), the sampling period could be subdivided into two periods either depending upon VOC composition in terms of Propy-Equiv fractions or surface winds. Elevated total VOC reactivity together with percentages of reactive components was found in the second period when air parcels passed by the sampling site from the well vegetated western area. As a consequence, a high degree of variability is found both in Propy-Equiv concentrations and the ratios of Propy-Equiv to carbon-atom based concentration. The smallest variability in reactivity related composition has been found in urban Shanghai, although wind direction varied and daily maximum wind speed ranged from $4\,m\,s^{-1}$ to $8\,m\,s^{-1}$ during the sampling period, implying dominant emission sources to be local and stable. The largest variability in VOC reactivity is found in Jinshan. This could be mainly explained by the distinct diurnal variation of isoprene, which rises to the highest level of about 4 ppbC around midday and falls to nearly zero at night, due to the variability of emission rate

ACPD
12, 9161–9194, 2012

in response to temperature and sunlight (Guenther et al., 1991, 1993). Since easterly winds generally dominate during the sampling period, hydrocarbons of anthropogenic origin display a very limited variation in the composition.

The relative ozone forming potential of individual species is assessed in terms of OH-reactivity weighted equivalent concentration (Table 2). The top 10 species account for at least about 70 % of total reactivity in all locations. At urban sites, the top species that are most relevant to ozone formation exhibit somewhat similar ranking, with m,p-xylene and toluene to be the most important. Consistent with results of previous investigation in urban Shanghai (Ran et al., 2009), total VOC reactivity is mainly contributed by aromatic species which are thought to be largely emitted by automobiles in urban centres. However, the relative importance of isoprene differs significantly, from negligible (ranked below 50th) in previous study to considerable (within top 5) in this study. The seasonal variation of vegetative cover as well as biogenic emission intensity should be responsible for such a difference between the annual isoprene average in previous study and summertime level in this study. Unlike in the urban areas, it is both the aromatic and alkene group that comprise most of the top 10 species in Wuqing. Isoprene is found to be most influential on total reactivity as also shown in Ran et al. (2011). This could be ascribed to strong isoprene emission in the well vegetated suburb and a much higher OH reactivity of isoprene compared to most anthropogenic species. Trans-2-butene and cis-2-butene could be associated with production of petroleum and manufacture of synthetic rubber. Their fractions amount to about 19 % of the total reactivity. Another particular aspect of top species in Wuqing is the importance of some industry related heavy alkanes like n-hexane, which is a widely used cleaning solvent in many industrial processes and also contained in gasoline and petroleum products. In the suburb of Shanghai, toluene is particularly important to total OH reactivity, followed by m,p-xylene and isoprene. The constituents of top species are almost exclusively aromatics and light alkenes. Given that Jinshan is a sparsely located residential area with low traffic loading, those reactive aromatic and alkene species except biogenic VOC isoprene should be attributed to emissions from the large petrochemical complex.

ACPD
12, 9161–9194, 2012

Last but not least, characterizations of VOC data involved in the discussion are subject to the impact of different sampling protocols in the four locations. This might lead to uncertainties in the analysis results to some extent. Long-term measurements with the same sampling duration and frequency would be critical to gain more detailed information on VOC characteristics and also be helpful in inferring emission sources from measured VOC composition.

3.3 Diurnal cycles of ozone and its precursors

As mentioned in Sect. 2, a subset of data is used here to discuss characteristics of ozone photochemical formation by examining average diurnal variations of ozone and its precursors under photochemistry-dominant conditions, except for VOC data that would be insufficient for analysis if only selected ones were considered.

In general, ozone concentrations undergo a diurnal pattern of reaching a maximum in the afternoon and a minimum in the early morning. A slight decline could be observed from midnight to the dawn in the polluted NCP and urban Shanghai (Fig. 5a), as a response to NO_x accumulation within the nocturnal planetary boundary layer. Nighttime NO_x concentrations remain such a high level (averagely ranging from about 20 ppbv to more than 30 ppbv among the three locations as shown in Fig. 5b) that enough depletion of ozone has been caused before sunrise. Occasionally, surface ozone could be completely consumed up by strong local NO emissions. On the contrary, nighttime ozone stays stably at about 20 ppbv in Jinshan, along with an average NO_x of 10 ppbv that reveals inconsiderable NO emissions and NO titration of ozone during the night. Ozone concentrations rise rapidly once photochemical processes start up. The large increase in surface ozone concentrations could also be attributed to vertical mixing that brings in above ozone-rich air in the residual layer. The turning point where ozone accumulation rates change from negative to positive values exhibits approximately 1-h delay (~ 06:30 a.m.) in urban Shanghai in comparison with other locations. Since fresh NO emissions are markedly strengthened during morning rush hours in urban areas, ozone accumulation is minimized or even completely inhibited due to NO consumption,

ACPD
12, 9161–9194, 2012

especially when VOC concentration and reactivity are not high enough to speed fueling ozone production as in the case of Xujiahui. Ozone concentrations increase with an observed accumulation rate ranging from 10–20 ppbv per hour preceding noon, arrive at its daily maximum in the afternoon and go down thereafter. The highest average daily maximum of nearly 110 ppbv is found in Wuqing, followed by a value of about 95 ppbv in urban Tianjin and Jinshan. The lowest average peak concentration is slightly over 80 ppbv in urban Shanghai. Averagely, the duration of hourly ozone concentrations that violate the threshold of 80 ppbv is the longest in Tianjin (~ 6 h), followed by Jinshan (~ 4 h) and urban Shanghai (only 1 h). On about 25 % of the observational days, daytime ozone exceedances (> 80 ppbv) lasted for more than 6 h in Tianjin region, while none were encountered in Shanghai. There were only 3 % of the observational days on which daily ozone exceedances lasted for 4 h at Xujiahui and 19 % at Jinshan. This reveals a more persistent ozone exposure risk in the Tianjin region than in Shanghai. Besides, it is notable that concurrent existence of high ozone and NO_x happened sometimes at night in Tianjin, as an evidence for regional mixing of aged air mass rich in NO_x and ozone in this polluted region.

Average ozone daily peak elevates from the urban center to the suburb in both regions. Calculated morning VOC/NO_x ratios are exclusively larger than 10 in suburban Tianjin and mainly between 8 and 10 in the urban center. At theses high VOC/NO_x ratios, the generation of net ozone is limited by the competition between the formation of organic nitrates by peroxy radicals reacting with NO/NO_2 and the pathway to form NO_2 by peroxy radicals reacting with NO (Finlayson-Pitts and Pitts Jr., 1986; NRC, 1991). Any reduction in available NO_x would limit the formation of ozone. However, organic nitrates often quickly undergo thermal decomposition in hot summer. Higher ozone production rates could still be expected under higher VOC reactivity. Thus, reactive VOCs abundantly released from a number of nearby industrial facilities in Wuqing possibly lead to the higher ozone peak in there than in the urban center. In the Shanghai region, a different story is told. Ozone formation has previously been found to be typically NO_x-inhibited in urban Shanghai (Geng et al., 2008; Ran et al., 2009), as also

ACPD
12, 9161–9194, 2012

indicated by measured morning VOC/NO_x ratios closely around 4 in this study. NO_x is mainly emitted by motor vehicles and greatly inhibits net ozone production. During the daytime, strong local traffic emission of NO helps maintain the highest NO_x concentration and the lowest ozone peak among all locations. The pronounced double peaks in NO_x diurnal variation are associated with heavy traffic during rush hours, causing ozone daily peak shifted to an earlier time. In the suburb of Shanghai, the level of VOCs is comparable to that in urban Shanghai, while NO_x concentrations are much lower and no diurnal variation is found. Calculated morning ratios of VOC/NO_x are variable from one chemical regime to another.

3.4 Ozone production rates

Model simulated ozone production rates for the four sites are shown in Fig. 6 as a function of NO_x concentrations. Apparently, the four curves that are calculated using the average VOC composition around midday at the four sites differ greatly. At each given NO_x concentration, the highest $P(O_3)$ is found in Wuqing, followed by Tieta, Xujiahui and Jinshan, which is in good agreement with the relative magnitude of their prescribed VOC reactivity in model runs. The discrepancies of $P(O_3)$ between the four locations increase with increasing NO_x concentration. Above several ppbv of NO_x, which is easily encountered in these areas, ozone production rates are found to be strongly dependent on VOC reactivity. This might explain in part the observed differences of photochemical ozone from one location to another. $P(O_3)$ undergoes similar variation in response to NO_x change at each site, that is to increase almost linearly at first and then go down after reaching the peak value. Albeit this similarity, the concentration of NO_x, to which maximum $P(O_3)$ corresponds, shifts from about 6 ppbv at Jinshan to 20 ppbv at Wuqing. As for specific simulation cases that rely on measurements made on a particular day, a considerable scatter has been found for each site, partly due to a difference in average and specific VOC composition and partly due to the use of measured NO instead of simulated one. In spite of the dispersion, case simulations for each site generally fall into the same chemical regimes except for that in Jinshan. According to the

ACPD
12, 9161–9194, 2012

model results, active ozone photochemical production presently found in Wuqing would burst into even more drastic enhancement when bumping into air parcels rich in NO_x. In the two urban centers, ozone production is more or less inhibited by high NO_x level. Ozone production seems to be highly variable in Jinshan, given the large variability of the VOC reactivity shown in Fig. 4. This implies detailed analysis for each specific case, favorably coupled with meteorology, is needed in this area.

Diurnal fractions of different VOC groups are examined in Fig. 7. The composition of VOC reactivity is relatively stable throughout the day in urban centers, while more variable in the suburbs as a result of isoprene emission in the daytime. Around midday, isoprene is of particular importance to fostering high ozone concentrations in the suburbs and less contributing in urban areas. High ozone production rates found in Wuqing should be ascribed to biogenic isoprene and industry related alkenes. As suggested in Ran et al. (2011), it would be more feasible to reduce anthropogenic emissions rather than background biogenic emissions for the purpose of ozone abatement, in particular, to make restriction criterions for industrial emissions. In both urban areas, aromatics that largely come from motor vehicles are considerably responsible for ozone formation. Since the derived ozone production rates depend on NO_x that is also mainly from automobile emissions in cities, a second thought should be given before implementing control strategies on automobile emissions that may lead to the migration of chemical regime. Although aromatics are key species related to ozone forming potentials in Jinshan on a daily average, it is isoprene that contributes most around midday when photochemical process is most active. Thereby, we suggest that even effective industrial emission reductions would be of little use to mitigate ozone pollution in this area.

4 Conclusions

A comparative study is carried out in this paper using a set of observational data at an urban and a suburban site in the megacities of Tianjin (NCP) and Shanghai (YRD),

ACPD
12, 9161–9194, 2012

as an effort to understand and handle current ozone problem in these fast developing megacities where a significant increase in ozone precursor emissions has been noted.

A distinction between the characteristics of ozone and its precursors has been found between Tianjin and Shanghai (Table 3). In the summer, high ozone concentrations (> 80 ppbv) of long duration (> 6 h) were frequently encountered in both urban and suburban Tianjin, while the occurrence of high ozone concentrations lasted for a shorter period (usually < 4 h) and had a much lower frequency in Shanghai, indicating more severe ozone pollution in the Tianjin region. Such differences in ozone behavior are thought to be largely attributed to higher VOC concentration and reactivity in Tianjin than in Shanghai. Model simulations based on measurements also reveal similar dependence of ozone production rates upon VOC reactivity.

On average, total VOC concentration as well as reactivity in Tianjin is approximately 2 to 3 times larger than that in Shanghai. VOC compositions in the two urban centers are to some extent similarly determined by emissions from automobiles and influenced by regional industrial sources. Industry related species like light alkenes and heavy alkanes are important components of total VOC mixture in suburban Tianjin, while aromatics dominate in suburban Shanghai. Although anthropogenic sources play a major role in contributing to total VOC concentrations, isoprene makes considerable contribution to total reactivity in the suburbs.

As for NO_x, the probability distributions in the two urban centers fairly resemble each other, with a peak corresponding to about 25 ppbv and an apparent tail over 50 ppbv. Strong local traffic emissions of NO in the daytime help maintain a high level of NO_x and exert an inhibition on ozone production in urban Shanghai. Distinct double-peak diurnal variations of NO_x have been observed on transport limited days as a result of heavy traffic during rush hours. In urban Tianjin where NO_x and VOC emissions are significant, observational analysis shows that ozone formation is sensitive to both precursors. In suburban Tianjin, NO_x concentrations are often below 25 ppbv, although polluted episodes with concentration exceeding 50 ppbv could also occasionally occur. Ozone production is completely restricted by available NO_x. With limited source

ACPD
12, 9161–9194, 2012

emissions in suburban Shanghai, NO_x concentrations remain close to about 10 ppbv without displaying a diurnal variation. The sensitivity of ozone photochemistry is found to be quite variable in this area.

Finally, we find that the ozone problem in Shanghai is on an urban scale. Stringent restrictions on local emissions would help reduce the occurrence of high ozone concentrations. By contrast, ozone pollution in Tianjin is a regional problem. Combined efforts to reduce ozone precursor emissions on a regional scale are urgently needed to bring the ozone problem under control. Future investigations involving more extensive observations would help to further our understanding of the ozone problem in these two megacities as well as extend the application of current conclusions.

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ACPD

12, 9161–9194, 2012

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ACPD

12, 9161–9194, 2012

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ACPD
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ACPD

12, 9161–9194, 2012

Table 1. Average mixing ratios and fractions of the three VOC categories at the four sites.

Sites / Conc.	Tieta		Wuqing		Xujiahui		Jinshan	
	ppbC	%	ppbC	%	ppbC	%	ppbC	%
Alkanes	113.2	36.6	231.8	52.9	54.4	44.8	24.3	24.4
Alkenes	24.5	7.9	37.3	8.5	4.7	3.9	4.1	4.1
Aromatics	171.9	55.5	169.6	38.6	62.3	51.3	71.2	71.5
Total	309.6		438.7		121.4		99.6	

ACPD
12, 9161–9194, 2012

Table 2. Top 10 species sorted by contributions to total OH reactivity at the four sites.

Tieta, urban Tianjin Species	%	Wuqing, suburban Tianjin Species	%	Xujiahui, urban Shanghai Species	%	Jinshan, suburban Shanghai Species	%
m,p-Xylene	20.0	Isoprene	16.0	m,p-Xylene	24.4	Toluene	31.5
Toluene	9.6	trans-2-Butene	10.6	Toluene	11.1	m,p-Xylene	16.5
trans-2-Butene	9.1	cis-2-Butene	8.1	Ethylbenzene	7.7	Isoprene	11.2
1,2,4-Trimethylbenzene	7.4	m,p-Xylene	7.5	Isoprene	5.0	1,3-Butadiene	5.4
cis-2-Butene	7.1	3-Methylhexane	6.0	o-Xylene	4.3	Ethylbenzene	3.7
Isoprene	4.9	n-Hexane	4.9	Propene	3.7	Propene	3.0
Propene	4.8	Toluene	4.8	n-Pentane	3.6	o-Xylene	3.0
Ethylbenzene	4.6	1,3,5-Trimethylbenzene	4.1	1,2,4-Trimethylbenzene	3.6	1,2,4-Trimethylbenzene	2.3
o-Xylene	3.5	1,2,4-Trimethylbenzene	4.1	Isopentane	2.9	trans-2-Butene	1.8
n-Pentane	3.1	1,2,3-Trimethylbenzene	3.4	trans-2-Butene	2.9	n-Hexane	1.8
Top 10 species	74.1	Top 10 species	69.5	Top 10 species	69.2	Top 10 species	80.2

ACPD
12, 9161–9194, 2012

Table 3. A summary for comparisons of ozone, NO_x and VOCs attributes in the four locations.

Items to make comparisons			Tianjin		Shanghai	
			Urban	Suburb	Urban	Suburb
Ozone	Pollution Episodes (> 80 ppbv)	Frequency	High	Markedly high	Low	Moderate
		Duration	Long (> 6 h)	Long (> 6 h)	Negligibly short	Relatively long
	Diurnal Variation	Startup	Dawn	Dawn	1 h delay	Dawn
		Peak Time	Around 15:00	Around 15:00	Shift to 1 h earlier	Around 15:00
NO_x	Background		Polluted	Moderate	Polluted	Clean
	Pollution Episodes	> 50 ppbv	Readily	Occasionally	Often	Barely
	Diurnal Variation	Double Peaks	Evitable	Evitable	Pronounced	Not found
VOCs	Concentration		High	High	Low	Low
	Reactivity		Moderate	High	Low	Low
	Composition	Key Groups	Aromatics	Aromatics	Aromatics	Aromatics
			Light alkenes	Light alkenes		Isoprene
				Isoprene		

ACPD
12, 9161–9194, 2012

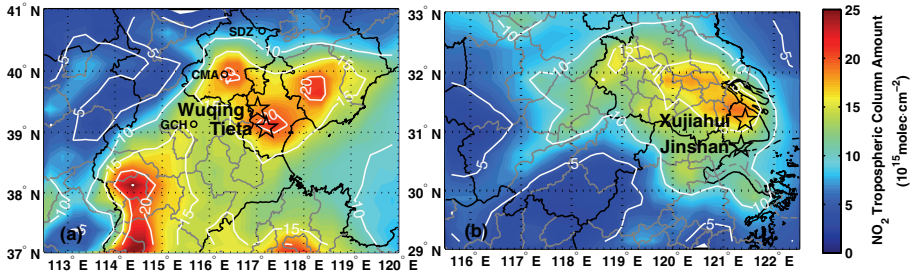

Fig. 1. Average NO_2 distributions during March 2009–2010 obtained from OMI (Ozone Measuring Instrument) Level 3 data in a resolution of $0.25^\circ \times 0.25^\circ$ **(a)** in the NCP; **(b)** in the YRD. The white lines are contour lines of NO_2 tropospheric column amounts. The black lines display the borders of provinces and coastlines. The grey lines show the borders of counties.

ACPD
12, 9161–9194, 2012

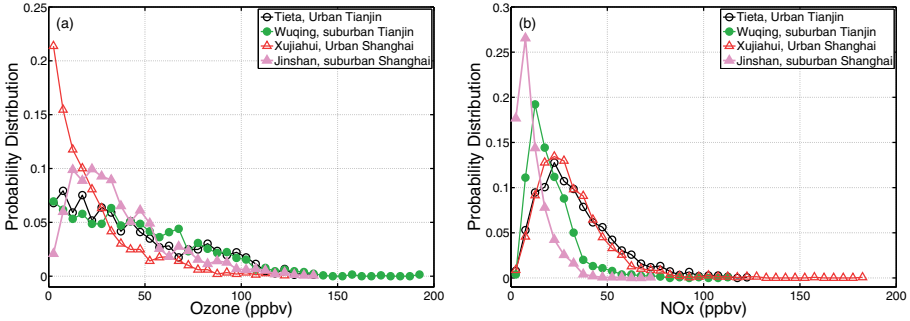

Fig. 2. Probability distributions (5 ppbv per bin) of **(a)** ozone and **(b)** NO_x in summer at the four sites.

ACPD
12, 9161–9194, 2012

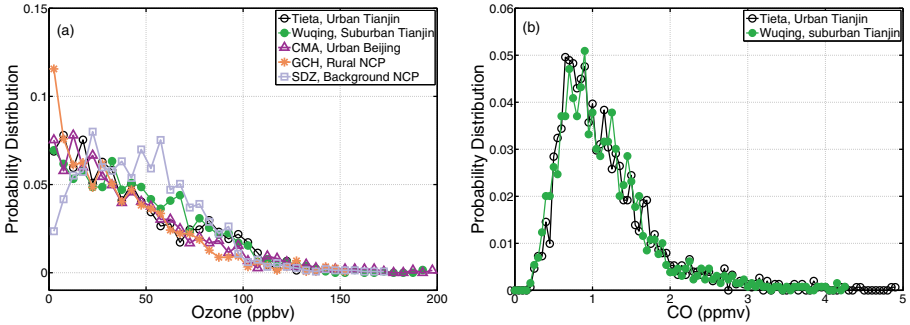

Fig. 3. Probability distributions of **(a)** ozone at five sites in the NCP (5 ppbv per bin); **(b)** of CO at both sites in Tianjin (0.05 ppmv per bin).

ACPD
12, 9161–9194, 2012

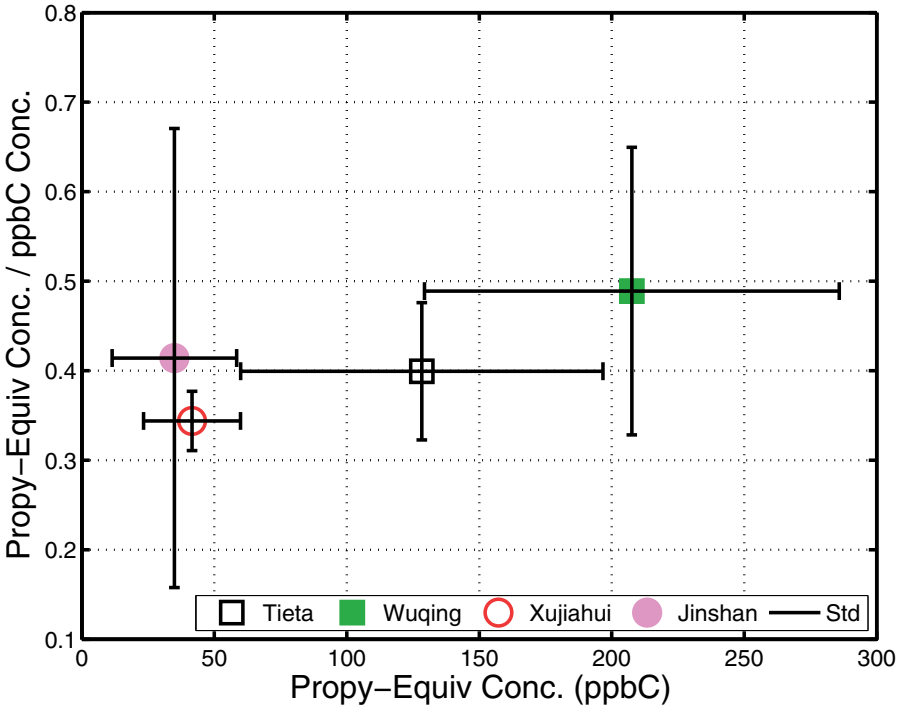

Fig. 4. VOC reactivity at each site of Tianjin and Shanghai. Dots represent average Propy-Equiv concentrations during the sampling period (x-axis), as well as the ratio of Propy-Equiv concentration to carbon-atom based concentration (y-axis). Standard deviations are given in black lines.

ACPD
12, 9161–9194, 2012

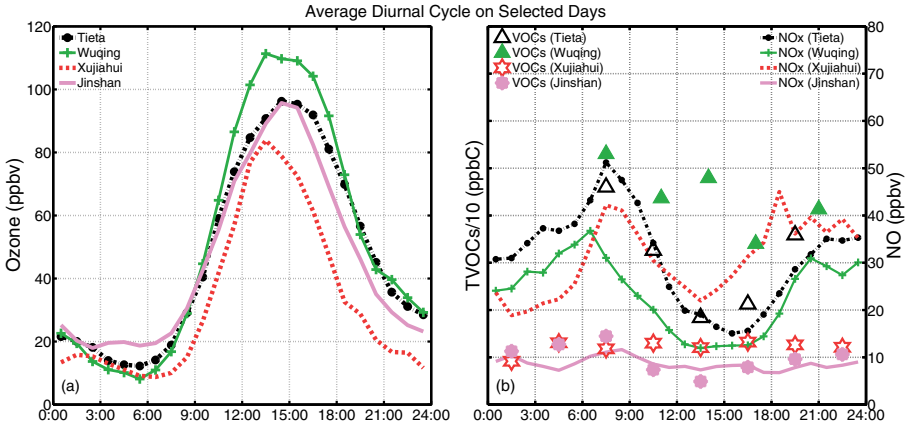

Fig. 5. Average diurnal cycles of **(a)** ozone and **(b)** its precursors on selected days.

ACPD
12, 9161–9194, 2012

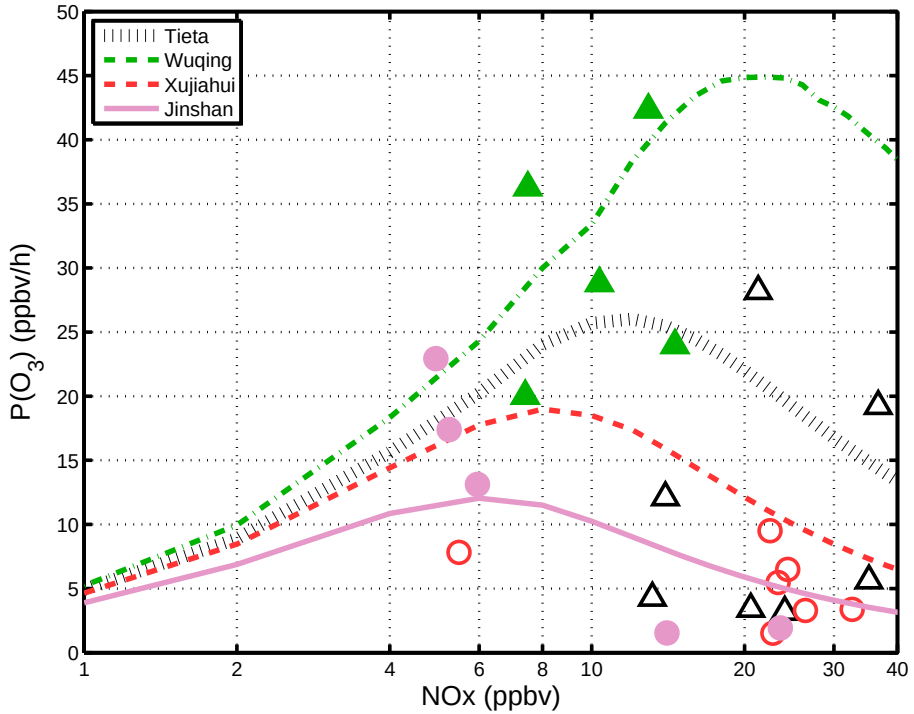

Fig. 6. Simulated instantaneous production rates of ozone (ppbv h^{-1}) as a function of NO_x (ppbv). Model results using the two chemical inputs are illustrated in the same colour for each site. Lines represent model results from prescribed NO_x concentrations and VOC measurements averaged over the whole sampling period. Markers represent model results from both measured NO_x and VOCs on each day of the sampling period if available.

ACPD
12, 9161–9194, 2012

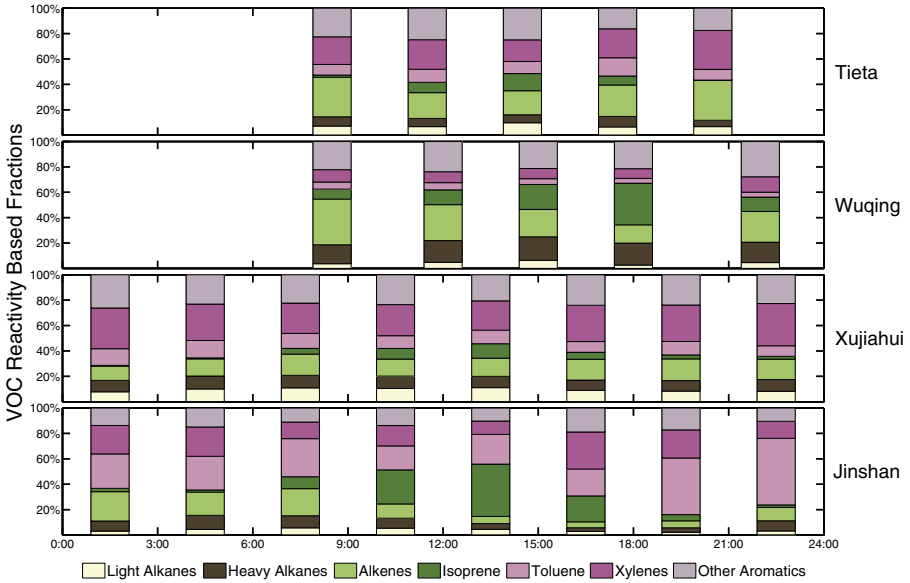

Fig. 7. Average diurnal fractions of different VOC groups at each site.

ACPD
12, 9161–9194, 2012