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

L. Ran[1,*], C. S. Zhao[1], W. Y. Xu[1], M. Han[2], X. Q. Lu[2], S. Q. Han[3], W. L. Lin[4,], X. B. Xu[4], W. Gao[5], Q. Yu[5], F. H. Geng[5], N. Ma[1], Z. Z. Deng[1,*], and J. Chen[1]**

[1]Department of Atmospheric and Oceanic Sciences, School of Physics, Peking University, Beijing, China
[2]Tianjin Academy of Environmental Sciences, Tianjin, China
[3]Tianjin Institute of Meteorological Science, Tianjin, China
[4]Chinese Academy of Meteorological Sciences, China Meteorological Administration, Beijing, China
[5]Shanghai Meteorological Administration, Shanghai, China
[*]now at: Key Laboratory of Middle Atmosphere and Global Environment Observation, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China
[**]now at: Meteorological Observation Center, China Meteorological Administration, Beijing, China

Correspondence to: C. S. Zhao (zcs@pku.edu.cn)

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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 non-methane hydrocarbons (NMHCs). Ozone pollution in summer was found to be more severe in the Tianjin region than in the Shanghai region, based on either the frequency or the duration of high ozone events. Such differences might be attributed to the large amount of highly reactive NMHCs in Tianjin. Industry related species like light alkenes were of particular importance in both urban and suburban Tianjin, while in Shanghai aromatics dominated. 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 probably 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 recently experienced an acceleration of economic growth and urbanization. Elevated anthropogenic emissions of primary gaseous pollutants have accordingly been noted in the last few decades, with a continuous increase to be foreseeable in the near future (Streets and Waldhoff, 2000; Klimont et al., 2001; Van der A et al., 2006, 2008). It is therefore not 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 volatile organic compounds (VOCs) that would photochemically generate ozone in the presence of sunlight, as has been well documented in a set of research articles (e.g.

Haagen-Smit, 1952; Haagen-Smit et al., 1953; Seinfeld and Pandis, 1998). Thus, there is an urgent need to tackle the ozone problem in these regions where precursor emissions significantly rise, in order to avoid possible threats to the public 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. In the NCP region, most observations and analysis were performed at regional background sites or in the megacity of Beijing (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, the 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 less successful 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 mainly 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 feasible and effective emission control strategies, more work needs to be done in these fast developing regions.

In this paper, observations regarding ozone and its precursors from an intensive field campaign in summer 2010 in urban Tianjin and from routine monitoring in summer 2009 in both urban and suburban Shanghai were comparatively analyzed and discussed, with the dataset from the 2009 Haze in China (HaChi) summer campaign in suburban Tianjin (Ran et al., 2011). This would hopefully cast more light on understanding and handling current ozone problem in the two megacities.

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. The suburban site Wuqing (39°23′ N, 117°01′ E) is the location where the 2009 HaChi summer campaign was carried out (site description refers to Ran et al., 2011). The site Xujiahui (31°12′ N, 121°26′ E) is a routine monitoring station in the crowded metropolitan area of Shanghai (Fig. 1b), which is overburdened with dense population, high traffic loading and numerous tower buildings. Near the coast and almost 50 km south of the urban center is a petrochemical industrial area, wherein the site Jinshan (30°45′ N, 121°21′ E) is situated. The residential population there is much less than in the urban center and the land cover is generally well vegetated.

To support 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 NO_x measurements, TEI 42CTL NO-NO_2-NO_x Analyzer at Wuqing simultaneously determined the ambient concentrations of NO and NO_x, 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 and the ECOTECH Oxides of Nitrogen Analyzer (EC9841B) used in urban areas of Tianjin and Shanghai were operated on the basis of similar techniques as TEI 42CTL. 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

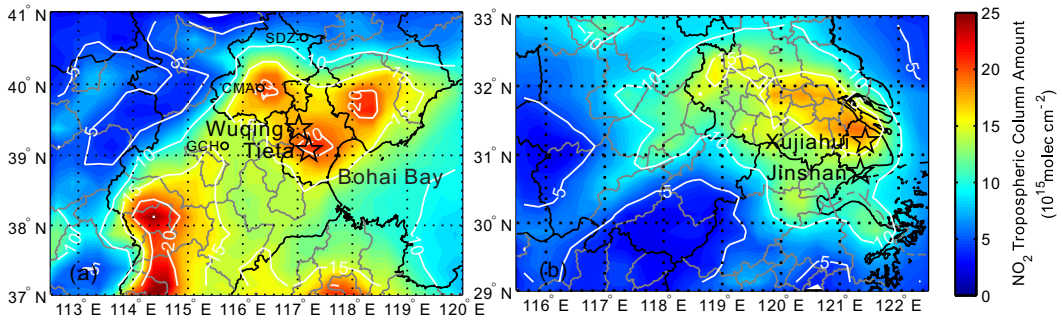

Fig. 1. Average NO_2 distributions during March 2009–2010 obtained from OMI (Ozone Measuring Instrument) Level 3 data in a resolution of 0.25° × 0.25° **(a)** in the NCP; **(b)** in the YRD. The white lines are contour lines of NO_2 tropospheric column amounts. The black lines display the borders of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

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 for each hour with at least 75 % valid data.

Sampling protocols of non-methane hydrocarbons (NMHCs) 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 LT) 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 LT) between 6 and 13 August 2009. An 8 l Teflon bag was used to collect instant air samples at a 30-min interval. Each 8 l air sample thus represents the average condition for the 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 on each day of 29 July to 6 August at Jinshan and 25 to 31 August at Xujiahui, respectively. Nonetheless, analytic methods for determining specific NMHC 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 (Agilent Tech., Ran et al., 2009) 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 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 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. Selected ozone and NO_x data are used in Sect. 3.3 to analyze their diurnal cycles 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 NMHCs 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,

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

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

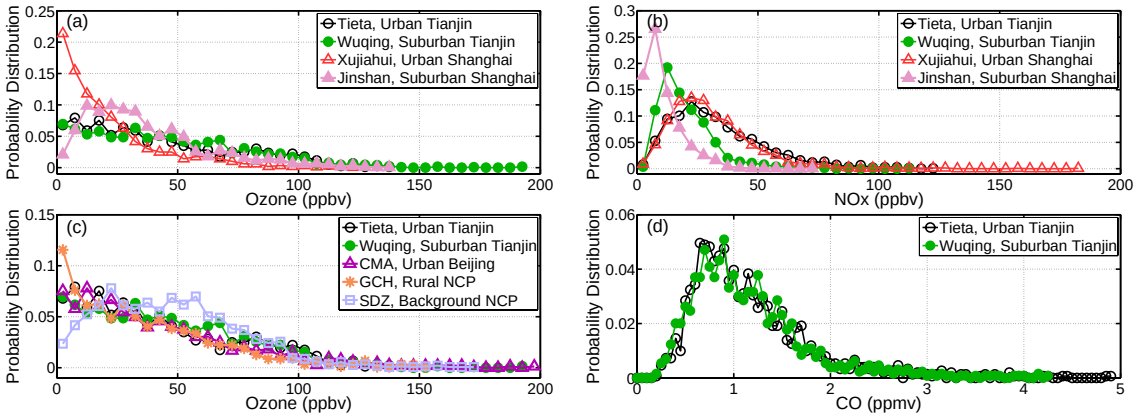

Fig. 2. Probability distributions of **(a)** ozone and **(b)** NO_x (both 5 ppbv per bin) in summer at the four sites; **(c)** ozone at five sites in summer 2009 in the NCP (5 ppbv per bin); **(d)** CO at both sites in Tianjin (0.05 ppmv per bin).

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 NCAR_MM (NCAR Master Mechanism, Version 2.3) 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, 1999). Model simulations are initialized by available measurements at 02:00 p.m. local time at each site. Each run lasts for half an hour for radicals to reach a steady state before losing initial information. Two types of chemical inputs are arranged. One is to average the midday NMHC data over the sampling period and adjust initial NO_x concentration for each run (1 ppbv and from 2 to 50 ppbv with an interval of 2 ppbv). The other is to perform a simulation for each NMHC sampling day by inputting midday NMHC 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 the model runs, peroxy radicals mainly react with NO to yield NO_2 in an amount given by the stoichiometric coefficients. At the end of each run, simulated HO_2 and RO_2 are used for $P(O_3)$ calculation according to 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 associated with high ozone episodes that pose threats to human health. A relatively higher probability of hourly ozone averages over 80 ppbv in Tianjin indicates more severe ozone pollution and a higher ozone exposure risk in summer in this region than in Shanghai.

A close similarity could be found in ozone probability distributions at both sites of Tianjin, implying a good 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 (Fig. 2c), especially at GCH, CMA, Wuqing and Tieta, which lie within a cluster of urban centers in the NCP. The frequency distributions of ozone daily maximum and ozone episode (1-h average > 80 ppbv) duration are generally similar among those sites, also suggesting ozone pollution in the NCP is probably a regional problem. This is consistent with the existence of a high-ozone belt peaking between Beijing and Tianjin demonstrated by Lin et al. (2009) on the basis of the regional distribution of ozone tropospheric column amounts. It is found that CO probability distributions at both sites of Tianjin are basically the same (Fig. 2d), also in support of well regional mixing of gas pollutants in the NCP. Nevertheless, an extended network of monitoring sites would be needed to provide more solid evidence for regional characteristics.

In contrast, ozone probability distribution in urban Shanghai is completely different from that in the suburb (Fig. 2a). Ozone probability distribution peaks at about 20 ppbv at Jinshan, while hourly averages are largely ($\sim$ 60 %) in the range of 0–20 ppbv at Xujiahui, where the frequency of ozone concentrations between 0 and 5 ppbv is even as high as 22 %. Strong NO emission from busy traffic should be most responsible for such a high frequency of very low ozone level in the downtown, in comparison with the suburban site Jinshan where fewer automobiles are there.

NO_x, as a short-lived species, is often characterized as more representative of local impacts than long-range

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

Conc. / Sites	Tieta Urban Tianjin		Wuqing Suburban Tianjin		Xujiahui Urban Shanghai		Jinshan Suburban Shanghai	
	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	

transport or regional mixing. Figure 1 displays the average distribution of tropospheric NO_2 columns from Ozone Measuring Instrument (OMI) in the NCP and YRD regions. OMI is a key instrument on NASA's Earth Observing System's (EOS) Aura satellite, with a spatial resolution of $13 \times 24\,km^2$ at nadir. OMI NO_2 Level 3 data used in this paper are gridded product with a horizontal resolution of $0.25° \times 0.25°$ in latitude and longitude. Generally, NO_2 (NO_x) pollution is more severe in the NCP than in the YRD. Besides, average distributions of OMI NO_2 exhibit differences in NO_2 concentrations within the megacity of Shanghai, in contrast to the high-NO_2 belt over the entire Tianjin-Beijing region. This might also imply that ozone issues in Tianjin are probably on a regional scale, while on an urban scale in Shanghai.

In-situ NO_x observations provide us 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 at suburban sites than urban sites. 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. At 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 at Jinshan, is almost zero at Wuqing. Polluted events with NO_x concentrations in excess of 50 ppbv could also be occasionally encountered in this area. As an industrial area near the transport hub inside the polluted NCP, Wuqing is apparently more polluted than Jinshan. In the 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 NMHCs

Average carbon-atom based concentrations of total NMHCs and each category in all locations are listed in Table 1. A higher level of total NMHCs is found in the Tianjin region (300–400 ppbC), about 2 to 3 times larger than the overall concentration in the Shanghai region. In both urban centers, automobile emissions undoubtedly make a substantial contribution to the NMHC composition. The traffic indicator methyl tert-butyl ether (Chang et al., 2003) is averagely about about 14 ppbC at Tieta and 6 ppbC at Wuqing, whereas 1.5 and 0.5 ppbC at Xujiahui and Jinshan, respectively (not shown in this paper). The NMHC 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 NMHCs are made up of alkanes at 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 %). Due to such large evaporation of heavy alkanes from industrial processes in this area, it is unsurprising yet noteworthy that total NMHC concentration at Wuqing is substantially larger than that at the urban site Tieta. The predominant component in Jinshan is the aromatic group (amounting to 72 %) that could be largely released from the process of petroleum refining. Toluene accounts for roughly 50 % of the mixture. As a matter of fact, carbon-atom based concentrations of toluene are very close (around 50 ppbC) at Jinshan, Tieta and Wuqing under the influences of petrochemical emissions. The ambient level of toluene at Xujiahui is only a half of that in other locations.

NMHC reactivity is more relevant to ozone formation in comparison with measured mixing ratio. Based on Propy-Equiv concentrations, the highest NMHC reactivity is found at Wuqing with a value of about 200 ppbC (Fig. 3). In urban Tianjin, average Propy-Equiv concentration of total NMHCs is about 130 ppbC. NMHC reactivities at both sites of Shanghai are less than one quarter of the NMHC reactivity at Wuqing and close to each other. The ratio of Propy-Equiv

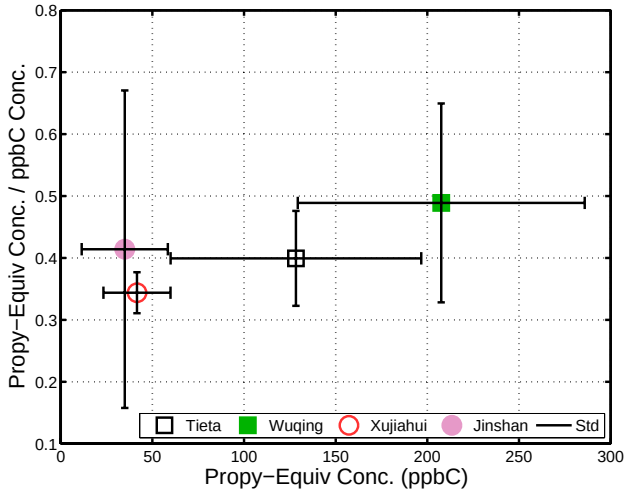

Fig. 3. NMHC reactivity at each site of Tianjin and Shanghai. Markers represent average Propy-Equiv concentrations during the sampling period (x-axis), as well as the ratio of Propy-Equiv concentration to carbon-atom based concentration (y-axis). Standard deviations are given in black lines.

concentration to carbon-atom based concentration could be treated as a simplified indicator for reactivity related composition. Such ratios (Fig. 3) reveal that the NMHC group at Wuqing consists of more reactive species. Reactivity compositions at Jinshan and Tieta are similar, leaving the share of reactive species in Xujiahui to be the lowest.

The variability of a dataset also has useful implications for data interpretation. Figure 3 gives standard deviations of both Propy-Equiv concentrations and the ratios of Propy-Equiv concentration to carbon-atom based concentration. 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 of reactivity related composition repeated every day, with a low valley in the afternoon. Large variability in Propy-Equiv concentrations is attributable to this diurnal variation. At Wuqing, the sampling period could be subdivided into two periods either depending upon NMHC composition in terms of Propy-Equiv fractions or surface winds (also see Ran et al., 2011). Elevated total NMHC 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 Xujiahui, 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 NMHC reactivity is found at 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 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, also see the average column in Fig. 6). The top 10 species account for at least about 70 % of the total reactivity in all locations. At urban sites, 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 Xujiahui (Ran et al., 2009), total NMHC reactivity is mainly contributed by aromatic species which are thought to be largely emitted by automobiles and solvent evaporation in urban centres (Lu et al., 2003; Song et al., 2007; Cai et al., 2010). 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 urban areas, it is both aromatic and alkene group that mainly constitute top 10 species at Wuqing. Isoprene is found to be most influential on the total reactivity. This was 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 might 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 at 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. At Jinshan, toluene is particularly important to total OH reactivity, followed by m,p-xylene and isoprene. The components of top species are almost exclusively aromatics and light alkenes, which should be emitted by the large petrochemical complex, given that Jinshan is a less populated residential area with relatively low traffic loading compared to the urban area.

Last but not least, characterizations of NMHC data involved in the discussion are subject to impacts of different sampling protocols at the four sites. 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 NMHC characteristics and also be helpful in inferring emission sources from measured NMHC composition.

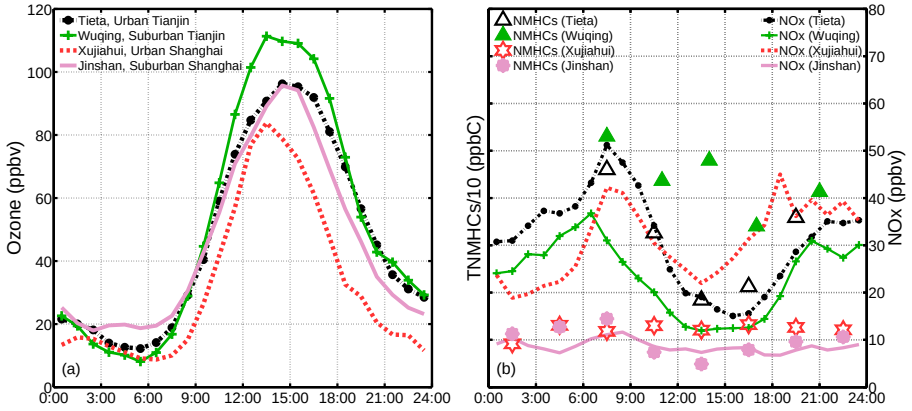

Fig. 4. Average diurnal cycles of **(a)** ozone and **(b)** its precursors on selected days (the selection criteria have been described in Sect. 2.2).

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

Tieta, Urban Tianjin		Wuqing, Suburban Tianjin		Xujiahui, Urban Shanghai		Jinshan, Suburban Shanghai	
Species	%	Species	%	Species	%	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

3.3 Diurnal cycles of ozone and its precursors

As mentioned in Sect. 2.2, selected ozone and NO_x data are used to discuss their average diurnal variations under photochemistry-dominant conditions. Average diurnal cycle of NMHCs during the sampling period is also examined for each site.

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. 4a), 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. 4b) that efficient 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 at Jinshan, along with an average NO_x of 10 ppbv that reveals low NO emissions and NO titration of ozone at night. Ozone concentrations rise rapidly once photochemical processes start up. The large increase in surface ozone concentrations could also be attributable to vertical mixing that brings in ozone-rich air from the residual layer aloft. 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, especially when NMHC concentration and reactivity are not high enough to accelerate 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 at Wuqing, followed by a value of about 95 ppbv at Tieta and Jinshan. The lowest average peak concentration is slightly over 80 ppbv at Xujiahui. 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 Xujiahui (only 1 h). On about 25 % of the observational days, the occurrence

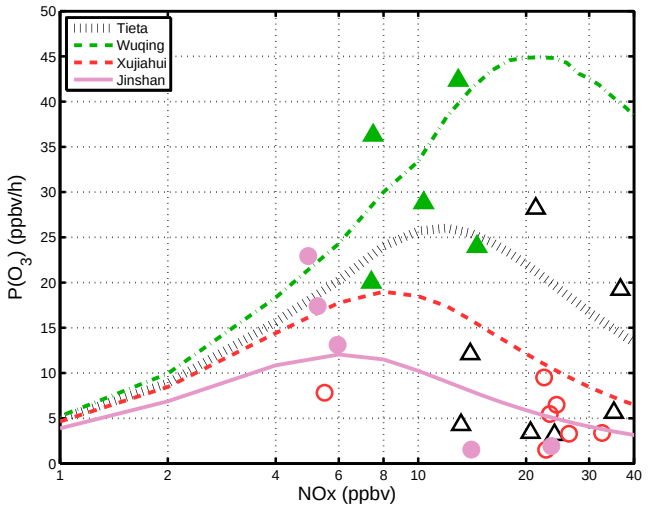

Fig. 5. Simulated instantaneous production rates of ozone (ppbv h^{-1}) as a function of NO_x (ppbv). Model results using the two chemical inputs are illustrated in the same colour for each site. Lines represent model results from prescribed NO_x concentrations and NMHC measurements averaged over the whole sampling period. Markers represent model results from both measured NO_x and NMHCs on each day of the sampling period if available.

of daytime ozone exceedances (> 80 ppbv) lasting for more than 6 h was observed in Tianjin region, while none was 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 increases from the urban center to the suburb in both regions (Fig. 4a). Calculated morning NMHCs/NO_x ratios are exclusively larger than 10 at Wuqing and mainly between 8 and 10 in the urban center (Fig. 4b). At theses high NMHCs/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 NMHC reactivity. Thus, reactive NMHCs 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 Xujiahui (Geng et al., 2008; Ran et al., 2009), as also indicated by measured morning NMHCs/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. At Jinshan, the level of NMHCs is comparable to that in urban Shanghai, while NO_x concentrations are much lower and no diurnal variation is found. Calculated morning ratios of NMHCs/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. 5 as a function of NO_x concentrations. The four curves that are calculated using the average NMHC composition around midday at the four sites differ greatly. At each given NO_x concentration, the highest $P(O_3)$ is found at Wuqing, followed by Tieta, Xujiahui and Jinshan, in good agreement with the relative magnitude of their prescribed NMHC 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 NMHC 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. The concentration of NO_x, to which maximum $P(O_3)$ corresponds, however 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 NMHC 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 model results, active ozone photochemical production 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 NMHC reactivity shown in Fig. 3. This implies detailed analysis for each specific case, favorably coupled with meteorology, is needed in this area.

Diurnal fractions of different NMHC groups are examined in Fig. 6. The composition of NMHC 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

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

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

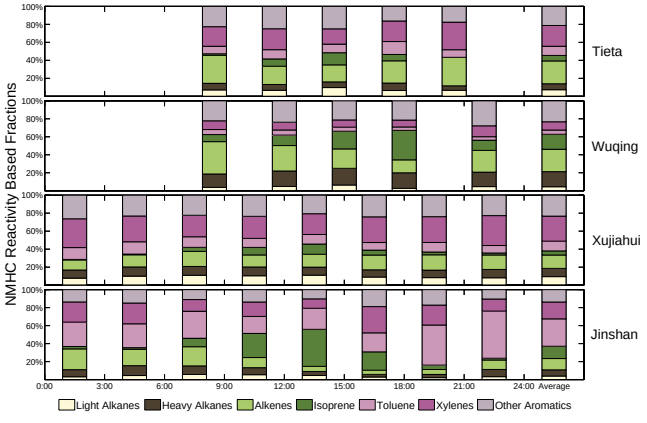

Fig. 6. Average diurnal fractions of different NMHC groups at each site.

to fostering high ozone concentrations in the suburbs and less contributing in urban areas. High ozone production rates found at 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 ozone production rates depend on NO_x and NMHCs, which are both largely 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), 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 attributable to higher NMHC concentration and reactivity in Tianjin than in Shanghai. Model simulations based on measurements also reveal similar dependence of ozone production rates upon NMHC reactivity.

On average, total NMHC concentration as well as reactivity in Tianjin is approximately 2 to 3 times larger than that in Shanghai. NMHC 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 NMHC mixture in suburban Tianjin, while aromatics dominate in suburban Shanghai.

Although anthropogenic sources play a major role in contributing to total NMHC concentrations, isoprene makes considerable contribution to total reactivity in the suburbs.

The probability distributions of NO_x in the two urban centers fairly resemble each other. Strong local traffic emissions of NO in the daytime 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 NMHC emissions are significant, observational analysis shows that ozone formation is sensitive to both precursors. At Wuqing, 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 emissions in Jinshan, 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, it is found that ozone problem extends over a larger area in the Tianjin region than in the Shanghai region based on both in-situ ozone measurements and OMI NO_2 observations. We thus conclude 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 probably 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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