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Ozone production in four major cities of China: sensitivity to ozone precursors and heterogeneous processes

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Abstract

Despite a large volume of research over a number of years, our understandings of the key precursors that control tropospheric ozone production and the impacts of heterogeneous processes remain incomplete. In this study, we analyze measurements of ozone and its precursors made at rural/suburban sites downwind of four large Chinese cities – Beijing, Shanghai, Guangzhou and Lanzhou. At each site the same measurement techniques were utilized and a photochemical box model based on the Master Chemical Mechanism (v3.2) was applied, to minimize uncertainties in comparison of the results due to differences in methodology. All four cities suffered from severe ozone pollution. At the rural site of Beijing, export of the well-processed urban plumes contributed to the extremely high ozone levels (up to an hourly value of 286 ppbv), while the pollution observed at the suburban sites of Shanghai, Guangzhou and Lanzhou was characterized by intense in-situ ozone production. The major anthropogenic hydrocarbons were alkenes and aromatics in Beijing and Shanghai, aromatics in Guangzhou, and alkenes in Lanzhou. The ozone production was found to be in a VOCs-limited regime in both Shanghai and Guangzhou, and a mixed regime in Lanzhou. In Shanghai, the ozone formation was most sensitive to aromatics and alkenes, while in Guangzhou aromatics were the predominant ozone precursors. In Lanzhou, either controlling NO_x or reducing emissions of olefins from the petrochemical industry would mitigate the local ozone production. The potential impacts of several heterogeneous processes on the ozone formation were assessed. The hydrolysis of dinitrogen pentoxide (N_2O_5), uptake of the hydroperoxyl radical (HO_2) on particles, and surface reactions of NO_2 forming nitrous acid (HONO) present considerable sources of uncertainty in the current studies of ozone chemistry. Further efforts are urgently required to better understand these processes and refine atmospheric models.

1 Introduction

Air quality in large cities has drawn increasing attention in recent years (Molina and Molina, 2004; Parrish and Zhu, 2009). A typical and intractable issue is photochemical smog characterized by unhealthily high concentrations of ozone (O_3) and other oxidants, which are products of atmospheric photochemistry involving volatile organic compounds (VOCs) and nitrogen oxides ($NO_x = NO + NO_2$). Despite a long history of control, photochemical smog remains a major environmental concern in large cities (Molina and Molina, 2004). The ozone problem is a complex coupling of primary emissions, chemical transformation, and dynamic transport at different scales (Jacob, 1999). A major challenge in regulating ozone pollution lies in understanding its complex and non-linear chemistry with respect to O_3 precursors (i.e., NO_x, CO and VOCs) that varies with time and from place to place. Therefore, investigating ozone pollution and the inherent chemistry in large metropolitan areas is critical from an environmental management point of view.

In recent decades China has become home to several megacities and many large cities owing to the fast-paced urbanization and industrialization processes. It is not surprising that these cities have been experiencing air quality deterioration, in view of the fast expansion in economics, energy use, and motor vehicles in the past decades. High ozone concentrations exceeding the national ambient air quality standards have frequently been observed in and downwind of large cities (e.g., Wang et al., 1998, 2001, 2006; Cheung and Wang, 2001; Zhang et al., 2007; Zhang et al., 2008; Ran et al., 2009). It has also been found that in some of the most urbanized regions, i.e., the north China plain (NCP), Yangtze River delta (YRD), and Pearl River delta (PRD), atmospheric ozone levels show an increasing trend over the last decade (Ding et al., 2008; Shao et al., 2006; Wang et al., 2009b; Xu et al., 2008). In view of the projected increase in emissions of NO_x and VOCs in the near future (Ohara et al., 2007), a worsening prospect of the ozone problem is foreseen and hence effective control strategies based on scientifically solid knowledge must be in place in order to return to clearer and cleaner skies.

A number of studies have been conducted to address the ozone pollution in China, mostly in the NCP, PRD, and to a lesser extent, the YRD regions. Overall, the results in Beijing have revealed that the ozone problem was serious but the formation chemistry was non-uniformly distributed within the city and with time. For example, Shao et al. (2009) reported a VOCs-limited regime of ozone production according to the relationship between the daily peak ozone and initial VOC concentrations at an urban site (Peking University; PKU) in the summers of 2004–2006. In comparison, Liu et al. (2012) suggested a transition regime based on a 1-D photochemical model constrained by measurements taken at the same site in summer 2007. Using an observation-based chemical box model, Lu et al. (2010) indicated that both VOCs-limited and NO_x-limited regimes existed at both urban (PKU) and suburban (Yufa) sites but the O_3 episodes at PKU were mostly sensitive to NO_x. Interesting results were obtained in summer 2008 when the Olympic Games were hosted in Beijing and unprecedentedly strict control measures were implemented (UNEP, 2009). The ozone levels were found to increase significantly after the full control despite the large reductions in NO_x and VOCs in Beijing, implying that the current control measures were less effective for ozone pollution (Chou et al., 2011; Wang et al., 2010b). Another hot spot of ozone research is the PRD region in southern China. Most studies have indicated consistently a VOCs-limited regime and the dominance of reactive aromatics in Guangzhou and Hong Kong (Zhang et al., 2007; Zhang et al., 2008; Wang et al., 2010c). However, most previous studies mainly focused on the autumn season during which the ozone problem is the most severe, less is known about the ozone chemistry in other seasons such as spring when the ozone pollution is also serious (Wang et al., 2009b). In recent years, several studies were also conducted in the YRD to investigate the ozone production processes. Tie et al. (2013) suggested a strong VOCs-limited regime not only in urban Shanghai but on a larger regional scale based on both observations and modeling analysis. Ding et al. (2013) investigated the relationship between O_3 and its precursors (CO and NO_y)

at a regional background site in Nanjing and suggested a VOC-limited regime in the region. Ran et al. (2009, 2012) carried out year-round measurements of O_3 and O_3 precursors at an urban and a suburban site, and suggested the predominant role of aromatics in ozone formation in Shanghai. However, a reactive VOC species, ethene, was not included in their observations.

Atmospheric models are common tools used to diagnose ozone formation regimes from the involute emission or measurement data. The chemical mechanisms underlying the models are usually simplified representations of the complex chemistry of the atmosphere, with the organic species of similar reactivities and structures grouped into one model species (e.g., Stockwell et al., 2012). This chemical lumping gives reduced computational runtimes in the application of mechanisms, but may produce extra uncertainties when applied to different atmospheric conditions (e.g., with different VOC emissions; the lumped mechanism is usually optimized for specific atmospheric conditions). The Master Chemical Mechanism (MCM) is a highly explicit mechanism that has the minimum amount of chemical lumping (Jenkin et al., 1997, 2003; Saunders et al., 2003), and thus is the best choice to investigate atmospheric photochemistry (including ozone production) for various environments. Another source of uncertainty in atmospheric photochemistry is heterogeneous chemical processes, which have recently been found to be more complex than previously thought. Several cases in point are the hydrolysis of dinitrogen pentoxide (N_2O_5), uptake of hydroperoxyl (HO_2) on particles, and the heterogeneous reactions of NO_2 forming nitrous acid (HONO) (Brown et al., 2006; Thornton et al., 2008; Su et al., 2011). These heterogeneous processes are believed to be more relevant in China given the very high aerosol loadings. To date only limited studies have attempted to address the potential impacts of these processes, and they suggest the important role of HO_2 uptake in ozone formation (e.g., Kanaya et al., 2009; Liu et al., 2012).

From 2004 to 2006, intensive measurements of O_3, O_3 precursors, and other related parameters were conducted in suburban/rural areas near four Chinese major cities, namely, Beijing, Shanghai, Guangzhou, and Lanzhou. These cities are located in different regions of China (see Fig. 1) and have different geographies, climates, industries, and emission patterns. The same measurement techniques were utilized in all these campaigns, making the inter-comparison among cities free from uncertainties due to differences in the methodology of observations. This paper analyzes the measurement data to examine the sensitivities of O_3 production to O_3 precursors and heterogeneous processes. We first present the overview of ozone pollution and hydrocarbon distributions observed at the four cities (Sect. 3.1). We then apply an observation-based MCM model (OBM) to the comprehensive data on twelve O_3 episodes, with the aim of assessing in-situ ozone production (Sect. 3.2) and its sensitivities to both ozone precursors (Sect. 3.3) and heterogeneous processes (Sect. 3.4).

2 Methods

2.1 Study areas and site locations

The field measurements were conducted in rural/suburban areas near three megacities in northern (Beijing), eastern (Shanghai) and southern (Guangzhou) China, and a large city (Lanzhou) in western China. The sampling sites were carefully chosen downwind of urban centers during the study periods to allow detailed examination of the regional-scale pollution and processes. These sites have been separately described in our previous studies (Wang et al., 2006; Gao et al., 2009; Zhang et al., 2009a; Pathak et al., 2009), and below we only give a brief outline.

Beijing is the capital city of China and one of the largest cities in the world. It is located on the northwestern edge of the densely populated North China Plain (see Fig. 1), and accommodates over 19 million inhabitants, 5 million automobiles, and many factories and power plants within an area of 16 800 km^2. The measurements were conducted in a rural mountainous area in Chang Ping district (CP; 40° 21′ N, 116° 18′ E, 280 m a.s.l), approximately 50 km north (generally downwind in summer) of the city center. The site was in a fruit farm growing peaches and apricots, with sparse population and anthropogenic emissions about 10 km away (Wang et al., 2006). The sampling was carried out from 21 June to 31 July 2005.

Shanghai is the largest city in China with a population of over 23 million. It also has more than 2 million vehicles, China's largest petrochemical complex, steel manufacturer, a seaport, and other industries. The study site was in the Taicang Meteorological Station (31° 27′ N, 121° 06′ E, 20 m a.g.l), which is about 45 km northwest of Shanghai. Although Taicang belongs to Jiangsu Province, it is often influenced by emissions from urban Shanghai under the prevailing southeasterly winds in summer monsoon seasons. Another feature of the site is the existence of some local sources including coal-fired power plants and some traffic from nearby roads (Gao et al., 2009). The measurement data taken from 4 May to 1 June 2005 were analyzed in the present study.

Guangzhou is a megacity of over 12 million people in southern China. It is in the center of the Pearl River Delta region, which has been a "world factory" for a wide range of consumer products. The measurements were taken at Wan Qing Sha (WQS; 22° 42′ N, 113° 33′ E, 17 m a.g.l.), a suburban area about 50 km southeast of downtown Guangzhou (Pathak et al., 2009). The observation data collected between 20 April and 26 May 2004 were analyzed in this paper. Thus the present study of ozone pollution in late spring can be compared with and supplements previous investigations in the PRD that focused on autumn (Wang et al., 2010c; Zhang et al., 2007; Zhang et al., 2008).

Lanzhou is a large city of over 3 million people and an industrial center in the interior western China. It is situated in a narrow valley basin in mountainous regions with an average altitude of 1520 m a.s.l. This unique topography, together with its petrochemical industry as well as vehicle emissions (0.2 million cars in 2006), makes it a typical "basin" of ozone pollution in summer. It was also the first place in China where photochemical smog was reported (in 1980s; Zhang et al., 2000). The measurement site was located in Renshoushan Park (RSP; 36° 8′ N, 103° 41′ E), a suburban mountainous area with some peach trees and other vegetation (Zhang et al., 2009a). The industrial zone (Xigu Petrochemical District) is located about 5 km to the southwest, and the urban center is about 15 km to the southeast. The measurement campaign was conducted from 19 June to 16 July 2006.

2.2 Intensive measurements

During the four intensive campaigns, O_3, CO, SO_2, NO and NO_y were continuously measured at a time frequency of 1 min along with collection of VOC canister samples. O_3 was measured by a commercial UV photometric analyzer (*Thermo Environmental Instruments (TEI), Model 49i*). CO was monitored by a non-dispersive infrared analyzer (*Advanced Pollution Instrumentation, Model 300EU*) with internal zeroing automatically done every two hours. SO_2 was detected with a pulsed UV fluorescence analyzer (*TEI Model 43c*). NO and NO_y were measured by using a chemiluminescence analyzer (*TEI Model 42cy*) equipped with an externally-placed molybdenum oxide catalytic converter to reduce NO_y to NO. Aerosol number concentration and size distribution (10 nm–10 µm) were measured in real-time by a Wide-range Particle Spectrometer (*MSP, WPS model 1000XP*) in Beijing, Shanghai, and Lanzhou. Meteorological parameters including temperature, pressure, relative humidity (RH), wind direction and speed, and solar radiation were also continuously measured. All the above measurement techniques and quality assurance/control procedures have been described elsewhere (Wang et al., 2003; Gao et al., 2009; Zhang et al., 2009a; Xue et al., 2011).

Methane (CH_4) and C_2-C_{10} non-methane hydrocarbons (NMHCs) were determined by collecting whole air samples in evacuated stainless steel canisters with subsequent analysis by gas chromatography with flame ionization detection, electron capture detection, and mass spectrometry (the analysis was undertaken in the University of California at Irvine). Two sampling strategies were adopted in our studies. Typically, one canister sample was collected at noontime each day, providing a thorough picture of daytime VOC pollution during the campaigns. On selected ozone episode days, multiple samples were taken generally every two hours from 7:00 to 19:00 (LT), allowing the detailed modeling analysis. A detailed description of the VOC sampling and analysis is given in the Supplement. Note that the same measurement techniques were applied in all the four campaigns, ensuring the minimum uncertainty due to the measurements in comparison of the results.

2.3 Observation-constrained chemical box model

An observation-based chemical box model was used to estimate the in-situ O_3 production and examine the sensitivity to precursors and heterogeneous processes. The model is largely similar to the one outlined in Xue et al. (2013). Briefly, it is based on the Master Chemical Mechanism (v3.2; http://mcm.leeds.ac.uk/MCM/), a highly explicit mechanism describing the degradation of 143 primary VOCs, containing ∼ 16 900 reactions of ∼ 5725 organic species as well as the latest IUPAC inorganic mechanism (Jenkin et al., 1997, 2003; Saunders et al., 2003). In addition, several heterogeneous processes including uptake of N_2O_5, NO_3 and HO_2 on particles and formation of HONO through reactions of NO_2 on the ground and aerosol surfaces are also taken into account (see Sect. 3.4 for details). Dry deposition of various inorganic gases, PANs, peroxides, carbonyls and organic acids are incorporated in the model from the recent compilation (Zhang et al., 2003). The mixing layer height affecting the dry deposition rates was assumed to vary from 300 m at night to 1500 m in the afternoon. Sensitivity runs with varying maximum mixing heights (i.e., 1000 and 2000 m) showed that the impacts on the modeling results were negligible (i.e., $< 3\,\%$ in net ozone production rates).

The observed concentrations of O_3, CO, SO_2, NO, H_2O, temperature, pressure, aerosol surface area and area-weighted radius, CH_4, and C_2-C_{10} NMHCs were averaged or interpolated with a time resolution of 10 min and used as inputs to constrain the model. The aerosol surface area and radius were calculated from the aerosol number and size distribution measurements. For Guangzhou where the aerosol size distribution data were not available, we used the average diurnal data of aerosol surface and radius determined from a similar suburban site in Hong Kong (Tung Chung, close to the Guangzhou site; see Fig. 1) in the same season (May 2012). For hydrocarbons for which the measurements were not in real-time, the time-dependent concentrations at

10 min resolution were estimated as follows. During the daytime (i.e., 07:00–19:00 LT) when multiple samples were taken, the data gaps were filled by time interpolation. The nighttime concentrations were calculated based on the regressions with CO (for most hydrocarbons other than isoprene) and temperature (for isoprene), for which continuous observations were available. Photolysis frequencies were calculated as a function of solar zenith angle within the model (Saunders et al., 2003), and were further scaled with the measured solar radiation. The model calculation was made for the identified O_3 episode days with 00:00 LT as the initial time. Before each simulation, the model pre-ran for nine days with constraints of the campaign-average diurnal data so that the model approached a steady state for the unmeasured species (e.g., NO_2, radicals and carbonyls).

The model read the measurement data every ten minutes to calculate the in-situ O_3 production and destruction rates. The O_3 production is primarily achieved through oxidation of NO by HO_2 (R1) and RO_2 (R2; a full list of reactions is given in Supplement), with the production rate ($P(O_3)$) calculated as:

$$P(O_3) = k_1[HO_2][NO] + \sum(k_{2i}[RO_2]_i[NO]) \quad (1)$$

The O_3 destruction is mainly contributed by O_3 photolysis (R3), reactions of O_3 with OH (R4), HO_2 (R5), and unsaturated VOCs (R6), NO_2 with OH (R7) and RO_2 (R8, forming PANs; note that the decomposition of PANs was subtracted), and NO_3 with VOCs (R9), heterogeneous losses of N_2O_5 (R10) and NO_3 (R11), and dry depositions. Thus the O_3 destruction rate ($L(O_3)$) can be estimated as:

$$\begin{aligned}L(O_3) = {} & k_3[O(^1D)][H_2O] + \{k_4[OH] + k_5[HO_2] + \sum(k_{6i}[VOC_i])\}[O_3] + k_7[OH][NO_2] \\ & + k_8[NO_2][RO_2] + 2\sum(k_{9i}[VOC_i])[NO_3] + 3\text{Heter. loss}_{N_2O_5} + 2\text{Heter. loss}_{NO_3} \\ & + \text{dry deposition} \quad (2)\end{aligned}$$

Then the net O_3 production rate can be determined from the difference between Eqs. (1) and (2). The sensitivity of O_3 production to changes of different O_3 precursors was also estimated using relative incremental reactivity (RIR), which is defined as the ratio of decrease in O_3 production rate to decrease in precursor concentrations. RIR can be used as a metric for the effect of a given emission reduction on O_3 concentrations at a site without a detailed knowledge on the emissions (Cardelino and Chameides, 1995).In the present study, 20 % changes in the input precursor concentrations were used.

3 Results and discussion

3.1 Overview of ozone pollution and hydrocarbon reactivity

Table 1 documents the overall ozone pollution conditions observed at the four cities during the intensive campaigns. All four cities suffered from high ozone pollution. At the rural site of Beijing (CP), eighteen ozone episode days (here defined as days when the peak hourly O_3 concentration exceeded 100 ppbv; 44 % of the total) were observed during the 6-week measurement period. The maximum hourly O_3 concentration was recorded at 286 ppbv, which is by far the highest value reported in China in the open literature (Wang et al., 2006). Such frequency of O_3 episodes and extreme O_3 levels highlight the severe problem in Beijing and surrounding areas. At the suburban site near Shanghai (Taicang), six ozone episode days (21 %) occurred during the 4-week campaign with the maximum hourly O_3 value of 127 ppbv observed. The problem in Shanghai seemed less severe than those in Beijing and Guangzhou. This is consistent with the results of Ding et al. (2013) which suggested that the ozone pollution in the YRD was relatively lighter than the NCP and PRD due to the titration effect of the much higher levels of NO_x. At WQS downwind of Guangzhou, seven episode days (19 %) were encountered throughout the 37 measurement days. The maximum hourly O_3 mixing ratio was determined at 178 ppbv. This indicates that the ozone problem is serious not only in autumn, but also in late spring in the PRD region. In Lanzhou

(RSP), in the 4-week campaign, eight ozone episode days (29 %) were observed, and the maximum hourly O_3 value was measured at 143 ppbv.

Figure 2 presents the average diurnal variations of O_3, CO, NO, NO_y, and solar radiation at the four cities. Fast increases in ozone concentrations during the daytime are clearly shown at all sites. CO and NO_y displayed a typical double-peak diurnal profile at CP, Taicang and WQS, suggesting that they were largely of traffic-related origins. A distinct single-peak pattern with enhanced levels of CO and NO_y in the early morning (8:00–9:00 LT) was observed at RSP in Lanzhou (Fig. 2d). This was due to the advection of pollution plumes from the industrial zone (i.e., Xigu district) to the study site, as evidenced by the dominant southwesterly winds observed in the morning (Zhang et al., 2009a). The NO_y levels measured at Taicang and WQS were of magnitude 20–50 ppbv, and the levels observed at CP and RSP were relatively lower (10–30 ppbv).

Figures 3 and 4 show the average OH reactivities of CO and hydrocarbons obtained at the four cities, and Table 2 summarizes the top-10 NMHC species with the highest reactivity (see Supplement for the calculation of OH reactivity). To facilitate analysis of the hydrocarbon speciation, the 50+ species were categorized into anthropogenic hydrocarbons (AHC; encompassing most species except isoprene and α/β-pinenes) and biogenic hydrocarbons (BHC; comprising isoprene and α/β-pinenes), with the AHC further grouped into four sub-categories: reactive aromatics (R-AROM; including all aromatics except benzene), alkenes (including all alkenes), alkanes with ≥ 4 carbons (C4HC), and low reactivity hydrocarbons (LRHC; including methane, ethane, propane, acetylene, and benzene). (The measured hydrocarbon species and their categorization are given in Table S1 in the Supplement).

At CP, the reactivity of hydrocarbons (AHC and BHC) was lower than that of CO. This is attributed to the fact that the site is located in a rural mountainous area with few local anthropogenic emissions, and further implies that the urban plumes had undergone extensive photochemical processing during transport and were less reactive when arriving at the site. Alkenes (35 %) and R-AROM (34 %) were the major reactive AHC sub-groups. At the other three suburban sites (Taicang, WQS and RSP), in comparison, the reactivity was clearly dominated by AHC. At Taicang, the reactive AHC was dominated by both alkenes (43 %) and R-AROM (39 %). At WQS, R-AROM was the dominant AHC class with an average contribution of 46 %. At RSP, alkenes played a predominant role and composed on average 70 % of the AHC reactivity. In particular, the propene and ethene levels were extremely high, both of which contributed 53 % of the AHC reactivity. The different AHC speciation observed among these sites suggests distinct emission patterns and implies different major ozone precursors in the four cities (further discussed in Sect. 3.3).

3.2 High ozone events: in-situ production vs. regional transport

The subsequent discussion is based on analysis of the selected high ozone events during which the most comprehensive data were collected (i.e., multiple daily VOC samples were taken), aiming at understanding the formation of ozone episodes in these cities. A total of twelve ozone episodes (3 per city; Beijing: 9, 26 and 30 July 2005; Shanghai: 7, 8 and 22 May 2005; Guangzhou: 18, 23 and 24 May 2004; Lanzhou: 5, 11 and 12 July 2006) were analyzed in the present study. (The time series of ozone and related parameters during these events are provided in the Supplement.)

The change of O_3 mixing ratios at a given location is a result of in-situ photochemistry coupled with regional transport (including both horizontal and vertical). The contributions from both processes can be either positive (i.e., production and import) or negative (i.e., destruction and export). Here we examined the contributions from in-situ photochemistry and regional transport to the observed O_3 pollution at the study sites. We first determined the rate of change in O_3 mixing ratios from the observed O_3 time profiles (R_{meas}). The in-situ net O_3 production rate (R_{chem}) was calculated every ten minutes by the OBM model as described in Sect. 2.3 (note that the dry deposition has been taken into account; see Eq. 2). Then the difference ($R_{\text{trans}} = R_{\text{meas}} - R_{\text{chem}}$) can be considered as the contribution from regional transport (note that the effect of atmospheric mixing was also included here). Figure 5 shows the time series of O_3 and contributions of in-situ production and regional transport for the typical ozone episodes at the four cities (the results were similar for other episodes for each city and are not shown).

We are particularly interested in knowing the relative role of in-situ photochemistry and transport in the extremely high ozone levels (up to the hourly value of 286 ppbv) observed at CP, a rural site downwind of Beijing. As shown in Fig. 5a, the in-situ photochemical production clearly dominated the ozone accumulation (i.e., from ∼ 40 to ∼ 100 ppbv) from early morning (6:00–7:00 LT) to noon (12:00 LT). In the afternoon, however, the O_3 mixing ratios increased sharply from ∼ 100 ppbv to ∼ 220 ppbv within less than two hours (14:00–15:00 LT), which cannot be explained by the local production. At that time, the in-situ ozone production had been weakened due to the relatively low levels of VOCs and NO_x (see Sect. 3.1). Thus such a sharp increase of ozone was attributed to the transport of urban plumes from Beijing that had undergone extensive photochemical processing and contained high amounts of produced ozone. This was a very typical case at CP in summer and can be reflected by the sharper O_3 increase at 14:00–16:00 LT in the campaign-average O_3 diurnal patterns (Fig. 2a). These results highlight the efficient export of Beijing urban pollution in the afternoon, which can adversely affect the vegetation and crop production in downwind areas.

In comparison, the in-situ photochemical production dominated the O_3 accumulation throughout the daytime at suburban sites downwind of Shanghai, Guangzhou, and Lanzhou. Very strong ozone production (up to 40 ppbv h^{-1}) was determined during episodes at these sites. Regional transport generally made a negative contribution (i.e., export) to the observed ozone pollution. This indicates that the air masses at these sites were reactive enough to sustain the observed ozone increase and even had potential to export the produced ozone to downwind regions. In the next section, we further examine the sensitivities of in-situ O_3 production to the major O_3 precursors in these three cities by the OBM-calculated RIRs.

3.3 Sensitivity to ozone precursors

Figure 6 shows the OBM-calculated daytime average RIRs for AHC, BHC, CO, and NO_x during the selected O_3 episodes at Taicang, WQS and RSP, and Fig. 7 shows the RIRs for the four AHC sub-groups. Overall, the ozone formation regimes were consistent among cases for each site but different among sites.

3.3.1 Shanghai – aromatics- and alkenes-controlled

For the episodes observed at Taicang, the in-situ ozone production was found to be highly VOC-sensitive, specifically AHC-controlled. Within the AHC, reactive aromatics dominated and alkenes also made a significant contribution. The RIRs for NO_x were generally negative except for the 7 May 2005 episode when it was essentially near zero. This suggests that reducing emissions of aromatics and/or alkenes would facilitate the mitigation of ozone pollution, yet reduction in NO_x emissions may aggravate the ozone problem.

The current knowledge on the ozone production regime in Shanghai is primarily from the measurements made by Ran et al. (2009, 2012). Based on the measurements at both an urban (Xujiahui) and a suburban site (Jinshan), they reported the predominant role of aromatics in the VOC reactivity and ozone formation potentials in Shanghai. The results obtained at Taicang in the present study agree in part with them on the significance of aromatics, but also reveal the important contribution from alkenes. This difference may be due to the different local VOC emissions near the study sites and/or the fact that ethene was not measured in Ran et al. (2009, 2012) but was included in our study. Despite the relatively low reactivity, the high abundances still made ethene the second most important reactive hydrocarbon species at our study site (see Table 2), and ethene alone made a considerable contribution to the hydrocarbon reactivity and ozone formation. Future measurements should include ethene in order to fully understand the ozone formation in Shanghai.

3.3.2 Guangzhou – aromatics-dominated

At WQS, the AHC was also the most limiting precursor in producing ozone (Fig. 6). Among the AHC, reactive aromatics were the predominant sub-group (Fig. 7). The RIRs for NO_x were negative or near zero. Most previous studies in the PRD region have demonstrated the dominant role of aromatics in ozone formation in the autumn season due to the wide usage of industrial solvents (Chan et al., 2006; Zhang et al., 2007; Liu et al., 2008). The ozone production regime determined in late spring at WQS is in line with the findings of the previous studies in autumn. This consistency also implies the homogeneous ozone formation chemistry in the PRD region and in typical ozone pollution seasons.

3.3.3 Lanzhou – mixed regime and the role of petrochemical industry

At RSP, the ozone formation was in a mixed regime with high RIRs calculated for both NO_x and hydrocarbons (Fig. 6). And in general NO_x showed higher RIRs than hydrocarbons. Alkenes were the most important AHC compounds responsible for the ozone production (Fig. 7). In particular, light olefins such as propene and ethene were the most abundant reactive species, both of which presented approximately half of the AHC reactivity (see Table 2). Such high levels of olefins are attributable to the industrial structure of Lanzhou. Lanzhou is a well-known petrochemical city in western China with the CNPC (China National Petroleum Corporation) Lanzhou Petrochemical Company and many small petrochemical plants located in its Xigu District. Light olefins are major components of emissions from the petrochemical plants (Ryerson et al., 2003). The mixed ozone formation regime implies a more flexible control strategy of ozone pollution in Lanzhou. Either reducing emissions of olefins (from the petrochemical plants) or cutting the NO_x emissions (from petrochemical and power plants and vehicles) could result in an efficient decrease in ozone formation. Furthermore, reducing NO_x emissions seems to be more efficient than controlling the anthropogenic VOCs alone in mitigating the ozone pollution, as suggested by the relatively higher RIRs of NO_x than AHC.

Applicability of the results: it is noteworthy that the present analyses are only based on the measurements at certain locales of target cities and during several ozone pollution episodes, thus the applicability of the results may be spatially and/or temporally limited. Actually, this limitation is inherent to such kind of studies based on observations at limited stations and/or during relatively short periods. Nonetheless, the present study should be a good effort as a cross-region comparative study since the same measurement techniques and chemical model are deployed. The findings will enrich the current understandings of the ozone chemistry in major cities of China, especially for Lanzhou and Shanghai where such kind of studies were relatively scarce. Further studies with extensive spatial and temporal coverage are needed to fully address the ozone pollution chemistry in large cities of China.

3.4 Sensitivity to heterogeneous processes

In this section, we assess the potential impacts of several poorly-understood heterogeneous processes on the ozone photochemistry by incorporating them in the model and conducting sensitivity analyses.

3.4.1 N_2O_5 hydrolysis

The N_2O_5 hydrolysis may affect ozone production as (1) it serves as an important O_x sink pathway (hydrolysis of each N_2O_5 destroys three molecules of O_x, i.e., 2 NO_2 and 1 O_3); and (2) nitryl chloride ($ClNO_2$), a hydrolysis product that usually accumulates at night, can enhance the next-day's ozone production through releasing both a chlorine atom (Cl) and NO_2 by photolysis (Cl can oxidize hydrocarbons and thus promote ozone formation). The hydrolysis rate is considered to be first order in the N_2O_5 concentration (Chang et al., 2011). In the present study, this process is parameterized in the MCM model as follows.

$$N_2O_5 \rightarrow (2-\phi)\cdot NO_3^- + \phi\cdot ClNO_2 \qquad k_{10} \tag{R10}$$

where, ϕ is the production yield of $ClNO_2$, and k_{10} is the first order rate constant and can be estimated by

$$k_{10} = \frac{1}{4} \times v_{N_2O_5} \times \gamma_{N_2O_5} \times S_{aero} \tag{3}$$

where $v_{N_2O_5}$ is the mean molecular speed of N_2O_5 and is calculated from gas kinetic theory (Aldener et al., 2006); $\gamma_{N_2O_5}$ is the reactive uptake coefficient of N_2O_5 on particle surfaces; S_{aero} is the surface area concentration of aerosols and is calculated based on the measured particle number size distributions. The current uncertainty of this process primarily lies in the uptake coefficient of N_2O_5 ($\gamma_{N_2O_5}$) and production yield of $ClNO_2$ (ϕ), which are highly variable and dependent on the aerosol composition, humidity, and temperature (Chang et al., 2011).The $\gamma_{N_2O_5}$ derived on real atmospheric particles from limited available field measurements were in the range of 0–0.04, while the range determined on a variety of "pure" aerosols in the laboratory was relatively larger (e.g., 0–0.1) (Chang et al., 2011, and references therein). In the present study, we chose a moderate value of $\gamma_{N_2O_5} = 0.03$ with no production of $ClNO_2$ ($\phi = 0$) in the base model. Sensitivity model runs were conducted with a higher $\gamma_{N_2O_5}$ (0.1) and also with different production yields of $ClNO_2$ ($\phi = 0.1$ and 0.6).

The potential impacts of N_2O_5 hydrolysis on ozone production are illustrated in Fig. 8 (with the results on 7 May 2005 in Shanghai as an example). The heterogeneous loss of N_2O_5 on aerosols indeed represents an important O_x loss pathway at nighttime (e.g., up to 75 % and 80 % at $\gamma_{N_2O_5} = 0.03$ and 0.1), but is only of minor importance during the daytime (e.g., < 4 % at both $\gamma_{N_2O_5}$ values; see Fig. 8a). Varying the $\gamma_{N_2O_5}$ value to 0.1 only resulted in changes of < 3 % in the calculated net ozone production rates compared to the base run. Thus the O_x loss via N_2O_5 hydrolysis should be less important for the daytime ozone formation near the surface.

However, the $ClNO_2$ produced/accumulated via N_2O_5 hydrolysis at night may considerably enhance the next-day's daytime ozone production. For example, a sensitivity model run with a lower production yield ($\phi = 0.1$) showed a nighttime $ClNO_2$ level of ~ 400 pptv and only ~ 3 % increase in the daytime-averaged net ozone production rate, but that with a higher production yield ($\phi = 0.6$) could give ~ 2500 pptv of $ClNO_2$ and ~ 14 % increase in ozone production (see Figs. 8b and 8c). This indicates that the nighttime heterogeneous process involving N_2O_5 is a considerable uncertainty in the current understanding of ozone photochemistry. Clearly, in-situ measurements of N_2O_5 and $ClNO_2$ are urgently required to better understand this process and to provide more realistic parameterizations of $\gamma_{N_2O_5}$ and ϕ which can be adopted in air quality models. We also conducted sensitivity model runs with 20 % reduction in NO_x or AHC at $\phi = 0.6$ and the ozone formation regimes estimated from the base runs remained.

3.4.2 Uptake of HO_2 by particles

The heterogeneous loss of HO_2 on particle surfaces can act as an efficient radical sink at high aerosol loadings and hence attenuate the ozone production (Kanaya et al., 2009). This process was included in the model by adding the following reaction.

$$HO_2 \rightarrow \text{products} \qquad k_{12} \tag{R12}$$

The reaction rate was assumed to be first order of the HO_2 concentrations. k_{12} is the reaction constant that can be calculated by

$$k_{12} = -\left(\frac{r}{D_g} + \frac{4}{\gamma_{HO_2} \times v_{HO_2}}\right)^{-1} S_{aero} \tag{4}$$

where r is the surface-weighted particle radius; D_g is the gas phase diffusion coefficient and is assumed to be 0.247 $cm^2\,s^{-1}$ (Mozurkewich et al., 1987); γ_{HO_2} is the uptake coefficient of HO_2 on particles; v_{HO_2} is the mean molecular speed of HO_2; and S_{aero} is the aerosol surface area concentration. In the present study, r and S_{aero} were calculated based on the measurement data of particle number size distributions. Similar to N_2O_5 hydrolysis, the uptake coefficient (γ_{HO_2}) is a parameter with large uncertainty and is related to aerosol composition, temperature, and RH (Thornton et al., 2008). The laboratory studies determined the γ_{HO_2} in the range of 0.01–0.2 for different types of non-metal aerosols at room temperature, with much higher values (> 0.2) measured on the Cu-doped aqueous surfaces (Mao et al., 2010, and references therein). Taketani et al. (2012) recently reported relatively large γ_{HO_2} values for ambient aerosols at Mt. Tai (0.13–0.34) and Mt. Mang (0.09–0.40) in China by regenerating the particles sampled on the quartz filter in the lab. Here we adopted a value of $\gamma_{HO_2} = 0.02$ in the base model, and changed it to 0.2 and 0.4 for the sensitivity runs.

The model-predicted net ozone production rates with different γ_{HO_2} values are shown in Fig. 9 (also with the results on 7 May 2005 in Shanghai as an example). Increasing the γ_{HO_2} would lead to considerable reductions in the net ozone production. For instance, the daytime average net ozone production rates dropped ~ 7 % and ~ 13 % when $\gamma_{HO_2} = 0.2$ and $\gamma_{HO_2} = 0.4$ compared to the base run ($\gamma_{HO_2} = 0.02$). This means that the uptake of HO_2 presents another large source of uncertainty in current studies of ozone chemistry, and more studies are needed to quantify the ambient γ_{HO_2} values in areas with high aerosol loading such as China. To check the possible interference of the assumed γ_{HO_2} value (i.e., 0.02) on the ozone formation regimes as discussed in Sect. 3.3, additional sensitivity model runs were conducted with 20 % reduction in NO_x or AHC at $\gamma_{HO_2} = 0.2$. The results suggest that the ozone formation regimes estimated from the base runs ($\gamma_{HO_2} = 0.02$) generally hold at high γ_{HO_2} values (figures not shown).

3.4.3 Heterogeneous reactions of NO_2 forming HONO

HONO is a key reservoir of the hydroxyl radial (OH) and thus plays a crucial role in atmospheric chemistry. Recent studies have indicated the possible existence of “missing” source(s) for daytime HONO, which cannot be reproduced by the current models only considering the homogeneous source from the OH + NO reaction (e.g., Su et al., 2008, 2011). It has been suggested that the photo-enhanced heterogeneous reactions of NO_2 on various surfaces should be an important source of HONO (Su et al., 2008; Li et al., 2010). In the present study, HONO was not measured but simulated within the model. In addition to the homogeneous source, the heterogeneous sources from reactions of NO_2 on the ground and aerosol surfaces were also taken into account in the base model by adopting the parameterizations used by Li et al. (2010). The reaction rates were assumed to be first order in the NO_2 concentration (Aumont et al., 2003), and the processes were simplified as follows.

$$NO_2 \longrightarrow HONO \qquad k_g \tag{R13}$$

$$NO_2 \longrightarrow HONO \qquad k_a \tag{R14}$$

k_g and k_a are the first order rate constants for the ground and aerosol surface reactions, and can be estimated as

$$k_g = \frac{1}{8} \times v_{NO_2} \times \gamma_g \times \left(\frac{S}{V}\right) \tag{5}$$

$$k_a = \frac{1}{4} \times v_{NO_2} \times \gamma_a \times S_{aero} \tag{6}$$

where v_{NO_2} is the mean molecular speed of NO_2; γ_g and γ_a are the uptake coefficients of NO_2 on the ground and aerosol surfaces; S/V is the effective surface density of the ground, and S_{aero} is the aerosol surface area concentration. Considering the photo-enhanced production of HONO from the surface reactions (George, 2005; Monge et al., 2010), higher values of γ_g and γ_a were used during the daytime than at night. For γ_g, we used a value of $\gamma_g = 1 \times 10^{-6}$ at nighttime, and increased it to 2×10^{-5} during the daytime with solar radiation less than $400\,W\,m^{-2}$. With more intense solar radiation, a higher γ_g value of $2 \times 10^{-5} \times$ (solar radiation/400) was used. As to γ_a, we chose a value of $\gamma_a = 1 \times 10^{-6}$ at nighttime, and increased it to 5×10^{-6} during the day. An effective surface area of 1.7 m^2 per geometric ground surface was used to calculate the S/V (Vogel et al., 2003).

We also conducted a sensitivity model run with only the homogeneous HONO source, which is the case of most current atmospheric models. The results are shown in Fig. 10 (with those on 24 May 2004 in Guangzhou as an example). We can see that including heterogeneous reactions of NO_2 indeed produces more HONO (Fig. 10a), which in turn can significantly enhance the ozone photochemical production ($\sim 13\,\%$; see Fig. 10b). This suggests that the heterogeneous processes of NO_2 play an important role in atmospheric photochemistry and need to be included in air quality models. In-situ measurements of HONO, which were not available in China until recent years, have shown surprisingly elevated daytime concentrations of HONO (up to the ppb level) in the PRD region (e.g., Su et al., 2008). Such high levels of daytime HONO cannot be explained by only including the above heterogeneous reactions of NO_2, and some additional sources have been proposed (e.g., Su et al., 2011). It is not known if this phenomenon was also the case at our study sites, however the identification of additional HONO source(s) and quantification of its impacts are beyond the scope of the present study. The analyses presented here clearly indicate that the surface reactions involving NO_2 at least present an important HONO source and can enhance the ozone production. Undoubtedly, in-situ measurements of HONO are critical for better understanding the atmospheric photochemistry including ozone formation, and further efforts are needed to determine the "missing" source(s).

4 Summary

Measurements of O_3, O_3 precursors and related parameters were made at a rural site of Beijing and suburban sites downwind of Shanghai, Guangzhou and Lanzhou. The data were analyzed with the aid of a MCM-based, observation-constrained chemical box model to understand the ozone production chemistry in these cities. The main findings are summarized as follows.

1. The four cities suffered from serious ozone problems. At the rural site downwind of Beijing, transport of "aged" urban plumes resulted in hourly ozone levels up to 286 ppbv. At suburban sites downwind of Shanghai, Guangzhou and Lanzhou, the observed ozone accumulation was dominated by the intense in-situ photochemical production.

2. The hydrocarbon speciation was different among the sites/cities. The dominant anthropogenic hydrocarbon species were alkenes in Lanzhou, aromatics in Guangzhou, and both alkenes and aromatics in Beijing and Shanghai.

3. The ozone production during ozone episodes was in a VOCs-limited regime in Shanghai and Guangzhou, and a mixed regime in Lanzhou. In Shanghai, the ozone production was most sensitive to aromatics and alkenes. In Guangzhou, it was most sensitive to the aromatics. In Lanzhou, either cutting emissions of olefins from the petrochemical plants or reducing NO_x would decrease the ozone production.

4. Heterogeneous processes including N_2O_5 hydrolysis, uptake of HO_2 on aerosols, and surface reactions of NO_2 are considerable sources of uncertainty in the current understanding of ozone photochemistry. Further efforts are urgently needed to determine these processes and improve air quality models.

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/13/27243/2013/acpd-13-27243-2013-supplement.pdf.

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Table 1. Overview of ozone pollution conditions in four large Chinese cities.

Site	Location	Observation Period	Number of O_3 episode days*	Maximum hourly O_3 (ppbv)
Beijing CP	116.30° E, 40.35° N	21 Jun–31 Jul 2005	18	286
Shanghai Taicang	121.10° E, 31.45° N	4 May–1 Jun 2005	6	127
Guangzhou WQS	113.55° E, 22.70° N	20 Apr–26 May 2004	7	178
Lanzhou RSP	103.69° E, 36.13° N	19 Jun–16 Jul 2006	8	143

[*] The ozone episode day is defined here as the one with the maximum hourly ozone exceeding 100 ppbv.

Table 2. The top-10 NMHC species by OH reactivity (s^{-1}) in four large Chinese cities.

Rank	Beijing-*CP*		Shanghai-*Taicang*		Guangzhou-*WQS*		Lanzhou-*RSP*	
	species	reactivity	species	reactivity	species	reactivity	species	reactivity
1	isoprene	0.82	xylenes	1.12	toluene	0.75	propene	2.27
2	ethene	0.24	ethene	0.52	xylenes	0.75	isoprene	2.19
3	xylenes	0.22	toluene	0.42	isoprene	0.44	ethene	1.49
4	toluene	0.16	trimethylbenzenes	0.36	ethene	0.34	*1,3*-butadiene	0.34
5	trimethylbenzenes	0.16	propene	0.35	trimethylbenzenes	0.32	*1*-butene	0.34
6	*i*-butene	0.13	*i*-butene	0.31	α/β-pinenes	0.30	trimethylbenzenes	0.27
7	*i*-pentane	0.08	isoprene	0.25	propene	0.26	*i*-pentane	0.22
8	propene	0.08	*trans*-2-butene	0.24	*i*-butene	0.23	*i*-butene	0.22
9	α/β-pinenes	0.06	*cis*-2-butene	0.21	ethylbenzene	0.20	*n*-butane	0.21
10	methylcyclopentane	0.06	*i*-pentane	0.18	*i*-pentane	0.11	*n*-pentane	0.20

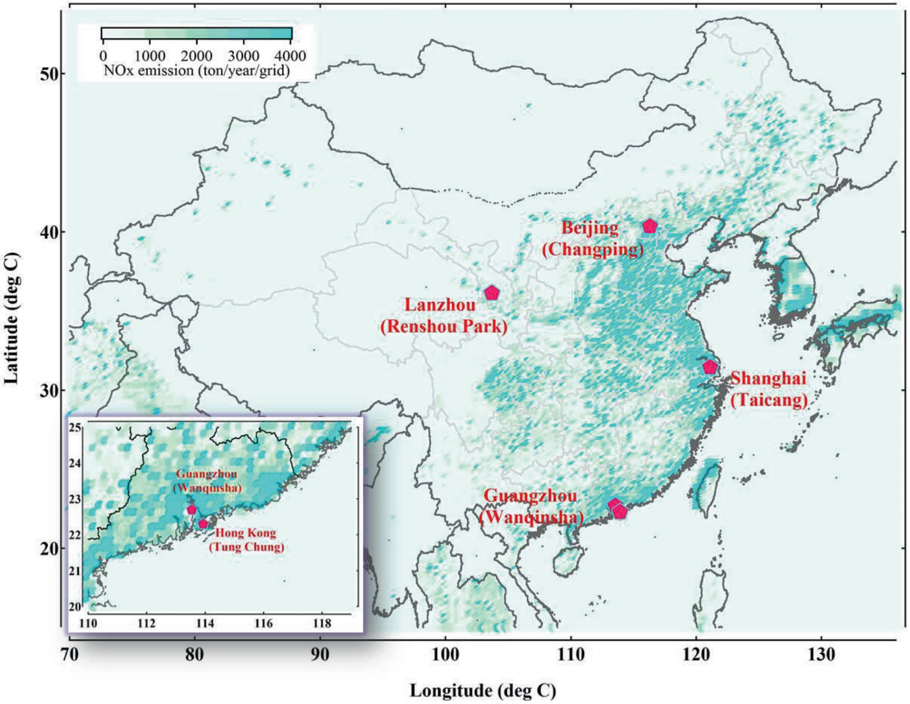

Fig. 1. Map showing the study areas and anthropogenic NO_x emissions over China. The emission data was obtained from Zhang et al. (2009b).

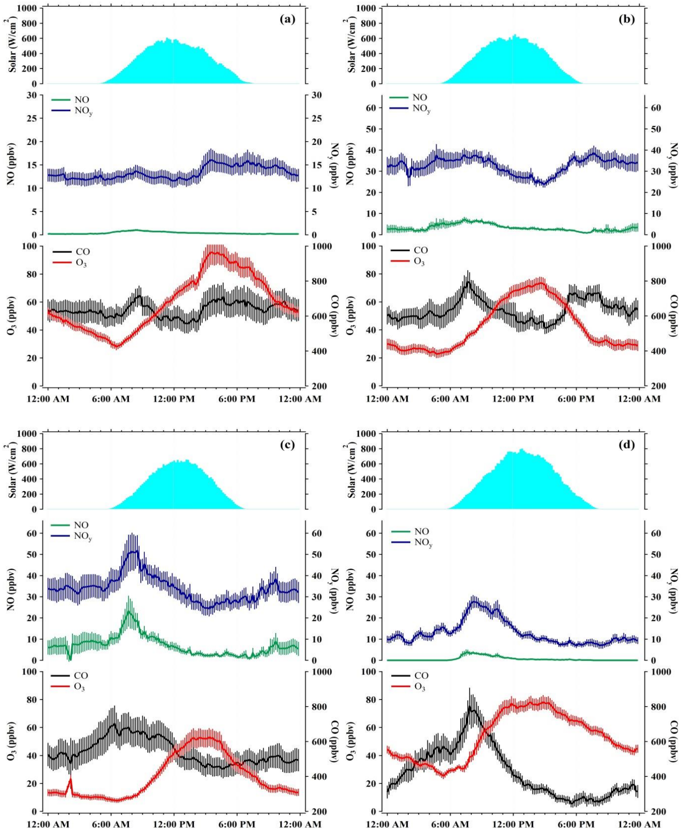

Fig. 2. Observed average diurnal profiles of O_3, CO, NO, NO_y, and solar radiation in **(a)** Beijing, **(b)** Shanghai, **(c)** Guangzhou, and **(d)** Lanzhou. The data time interval is 10 min, and error bars refer to the standard error.

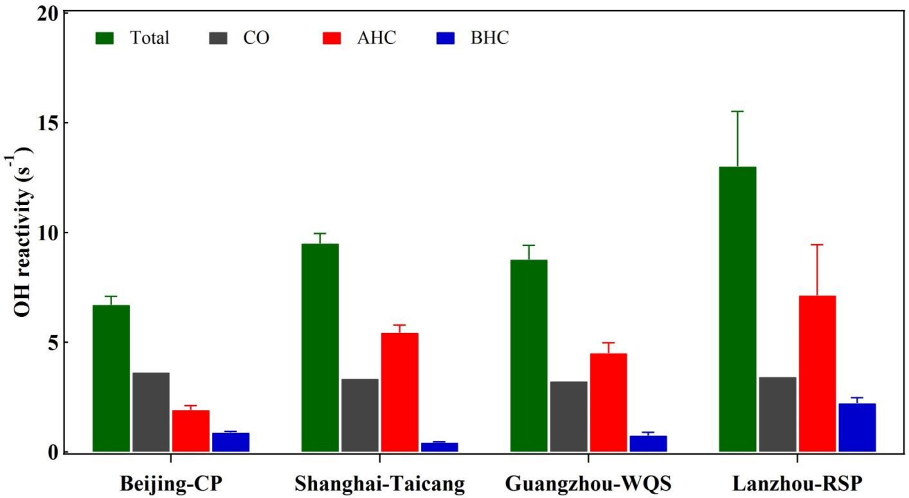

Fig. 3. Average OH reactivities of CO, anthropogenic hydrocarbon (AHC), biogenic hydrocarbon (BHC) and the total at the four cities. The error bars refer to the standard error.

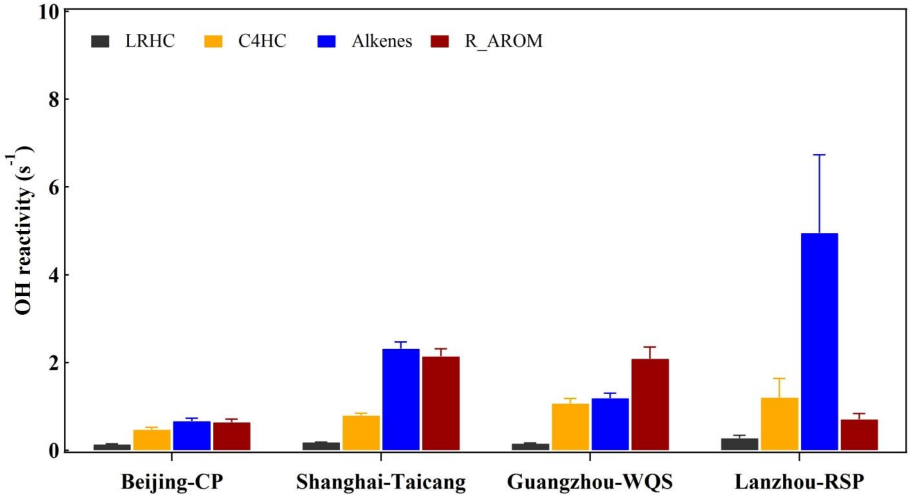

Fig. 4. The same Fig. 3 as but here for the four AHC sub-groups.

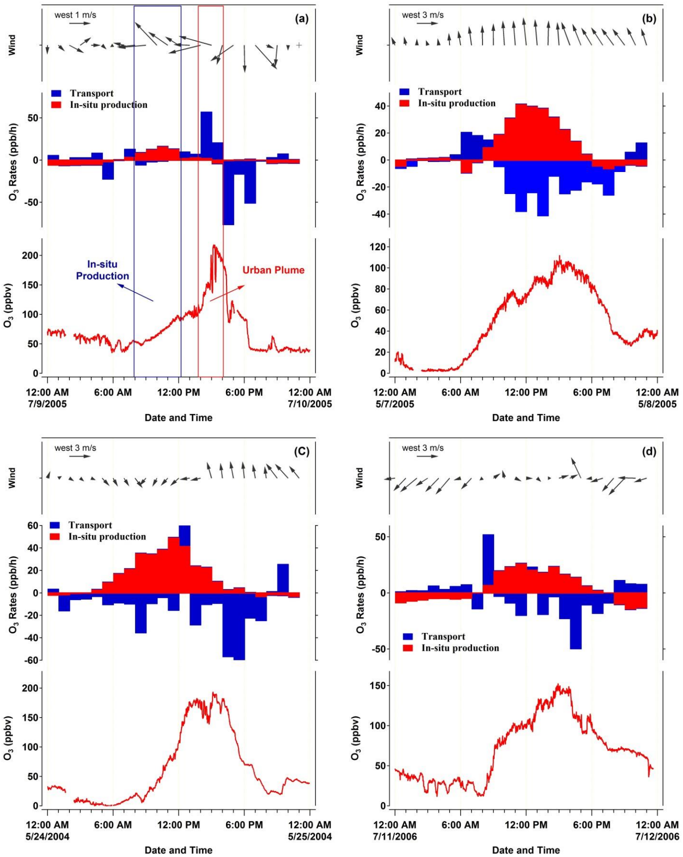

Fig. 5. Accumulation of O_3 and contributions from in-situ photochemistry and transport during O_3 episodes in **(a)** Beijing (9 July 2005), **(b)** Shanghai (7 May 2005), **(c)** Guangzhou (24 May 2004), and **(d)** Lanzhou (11 July 2006).

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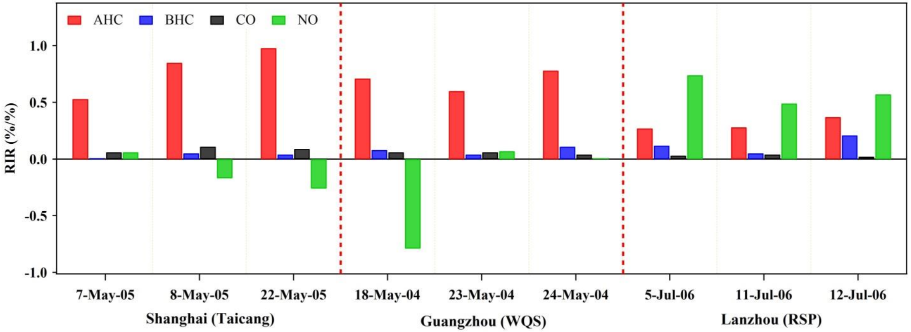

Fig. 6. The OBM-calculated RIRs for major ozone precursors during high ozone events in Shanghai, Guangzhou and Lanzhou.

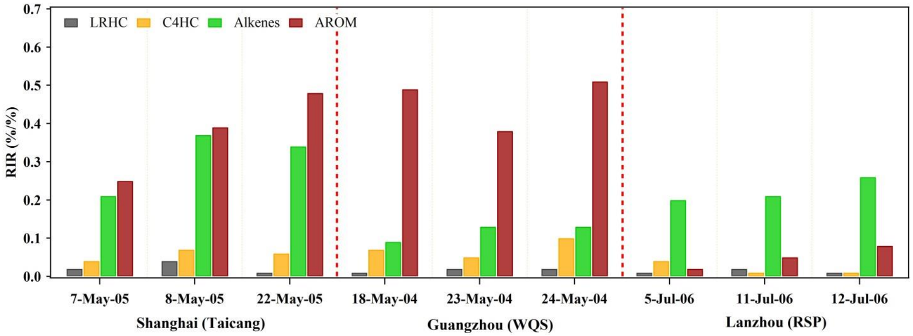

Fig. 7. The same Fig. 6 as but here for the four AHC sub-groups.

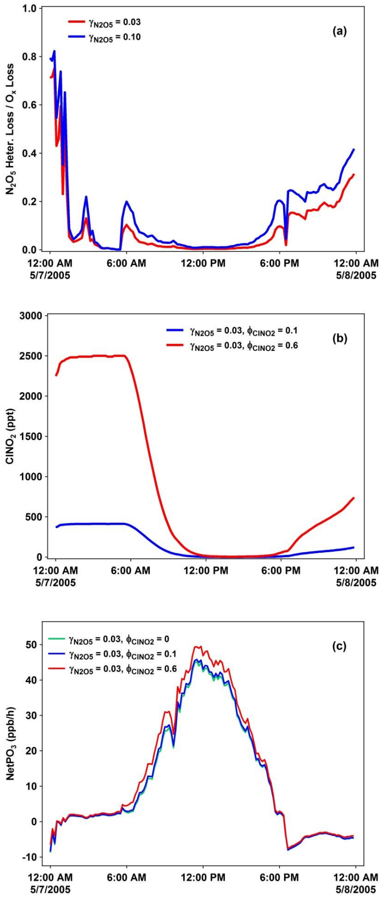

Fig. 8. (a) The contributions of N_2O_5 hydrolysis to the total O_x loss, **(b)** model-simulated $ClNO_2$ mixing ratios, and **(c)** net ozone production rates with different $\gamma_{N_2O_5}$ and ϕ_{ClNO_2} values on 7 May 2005 in Shanghai.

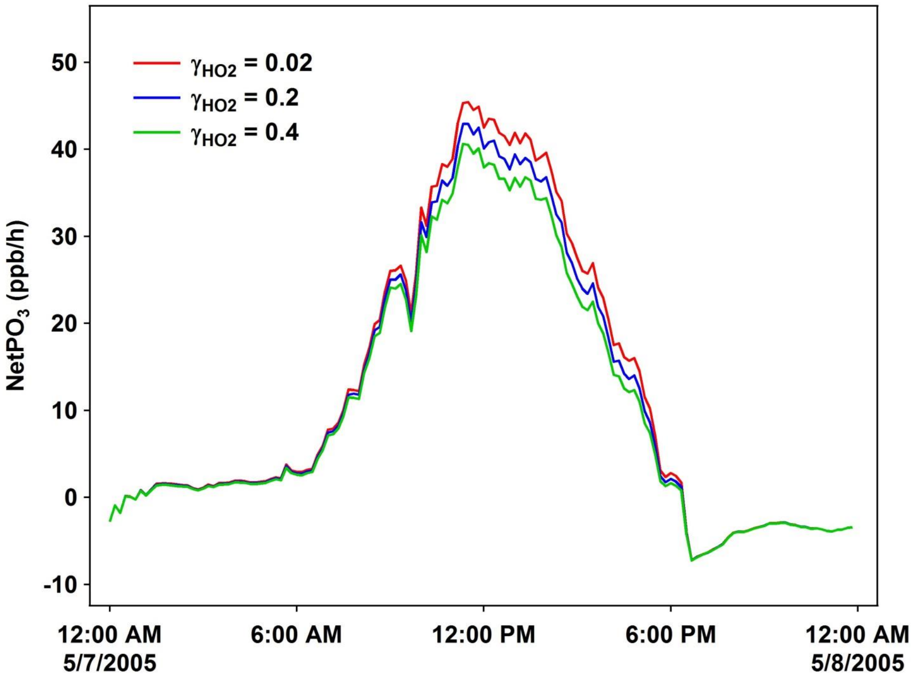

Fig. 9. The OBM-calculated net ozone production rates with different γ_{HO_2} values on 7 May 2005 in Shanghai.

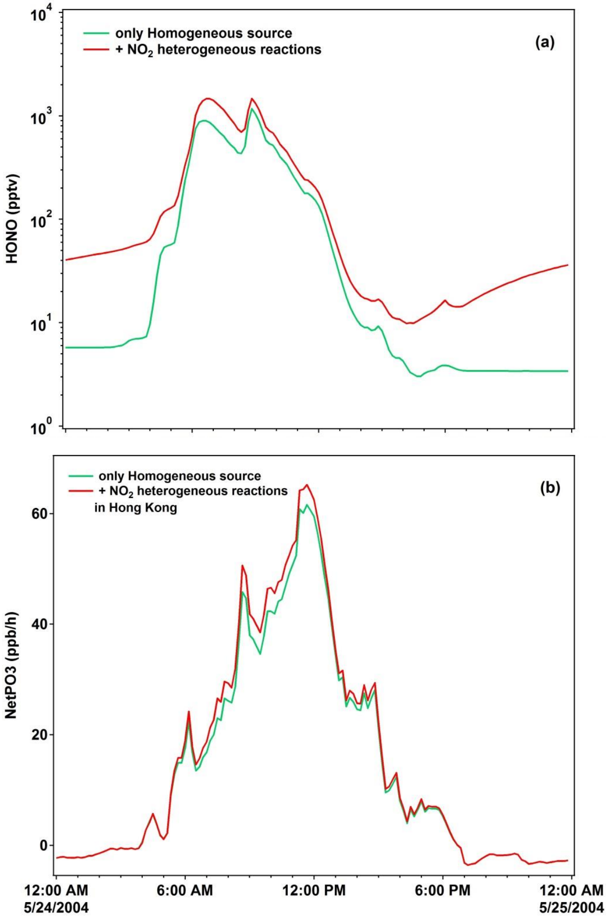

Fig. 10. **(a)** The model-simulated HONO mixing ratios and **(b)** net ozone production rates with and without heterogeneous reactions of NO_2 on ground/aerosol surfaces on 24 May 2004 in Guangzhou.