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Strong ozone production at a rural site in the North China Plain: Mixed effects of urban plumes and biogenic emissions

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ABSTRACT

Regional ozone (O_3) pollution has drawn increasing attention in China over the recent decade, but the contributions from urban pollution and biogenic emissions have not been clearly elucidated. To better understand the formation of the regional O_3 problem in the North China Plain (NCP), intensive field measurements of O_3 and related parameters were conducted at a rural site downwind of Ji'nan, the capital city of Shandong province, in the summer of 2013. Markedly severe O_3 pollution was recorded, with the O_3 mixing ratios exceeding the Chinese national ambient air quality standard on 28 days (a frequency of 78%) and with a maximum hourly value of 198 ppbv. Extensive regional transport of well-processed urban plumes to the site was identified. An observation-constrained chemical box model was deployed to evaluate *in situ* photochemical O_3 production on two episodes. The results show that the *in situ* formation accounted for approximately 46% of the observed O_3 accumulation, while the remainder (~54%) was contributed by regional transport of the O_3-laden urban plumes. The *in situ* ozone production was in a mixed controlled regime that reducing either NOx or VOCs would lead to a reduction of ozone formation. Biogenic VOCs played an important role in the local ozone formation. This study demonstrates the significant mixed effects of both anthropogenic pollution from urban zones and biogenic emission in rural areas on the regional O_3 pollution in the NCP region, and may have general applicability in facilitating the understanding of the formation of secondary pollution over China.

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Introduction

Air pollution has become a major public issue in recent years in China (Chan and Yao, 2008). The main concerns include haze marked by elevated concentrations of $PM_{2.5}$ in winter and photochemical smog characterized by high levels of ozone (O_3) in summer (Huang et al., 2015; Xue et al., 2014b). The recent national air quality monitoring report demonstrated that O_3 has overtaken $PM_{2.5}$ to become the top air pollutant in summer in the major urbanized regions of China (MEP, 2015). Ground-level O_3 at high concentrations poses a great threat to human health by inducing respiratory disease, and is also detrimental to crops and other vegetation (National Research Council, 1991; Monks, 2005). Consequently, mitigation of O_3 pollution is an essential part of the prolonged "battle" against air pollution in China.

In the troposphere, ozone is primarily produced from the chemical reactions of nitrogen oxides (NO_X = NO + NO_2) and volatile organic compounds (VOCs) in the presence of sunlight (Crutzen, 1973). It is well known that the photochemical formation of ozone is non-linearly dependent on its precursors (*i.e.*, NO_X and VOCs) and subject to influences from both local and distant sources, factors which complicate the control of ozone pollution (Trainer et al., 1993; Xue et al., 2014b). In China, fast urbanization and industrialization processes have produced increasing anthropogenic emissions of NO_X and VOCs, which have led to a significant rise in the levels of ambient O_3 and in the frequency of severe O_3 pollution in and downwind of major metropolitan areas (Ding et al., 2008, 2013; Pan et al., 2015; Wang et al., 2009; Xu et al., 2008, 2017; Xue et al., 2014b; Zhang et al., 2014; Sun et al., 2016). There are also abundant biogenic sources in rural areas, which might release highly reactive VOCs (*e.g.*, isoprene and monoterpenes) and thus contribute to regional O_3 formation (Tang et al., 2007; Xu et al., 2011; Zhang et al., 2007, 2008). The establishment of an effective control policy for regional O_3 pollution requires a thorough understanding of the O_3-precursor relationships, local versus regional contributions, and the effects of isolated urban emission and regional biogenic sources.

The North China Plain (NCP) is the most urbanized region of northern China. It is home to a number of emerging large cities that are surrounded by vast rural areas (see Fig. 1). Many studies focusing on the issue of air quality have confirmed the severity of photochemical pollution in this region and have attempted to track the formation mechanisms, including O_3-precursor relationships and local versus regional contributions (Chou et al., 2011; Huang et al., 2015; Kanaya et al., 2009; Liu et al., 2012; Meng et al., 2009; Pan et al., 2015; Ran et al., 2012; Wang et al., 2006, 2010; Xu et al., 2011; Xue et al., 2014b). Despite significant progress, most of these studies were conducted in or around the megacity of Beijing with fewer efforts focused on the other areas, especially the central and southern NCP which are generally located upwind of the Beijing area in summer (*e.g.*, Kanaya et al., 2009). Furthermore, the effects on regional ozone pollution of both anthropogenic emissions in the urban zones and biogenic sources in the rural areas have not been well quantified.

To better understand the formation of regional O_3 pollution in the NCP region, intensive field observations were conducted in a rural area in the summer of 2013. The study site was carefully chosen and was situated close to and downwind of Ji'nan, a large city in the central NCP. Very serious O_3 air pollution was documented in the present study. Analysis of observational data revealed the contributions from both regional transport of urban plume and *in situ* photochemical O_3 formation, and detailed chemical box modeling analyses suggested the important contributions of biogenic VOCs to the local O_3 production. In the following discussion, we first provide an overview of observations describing the characteristics of O_3 and O_3 precursors; we then use case studies to demonstrate the effects of urban plume and *in situ* O_3 formation; and finally we

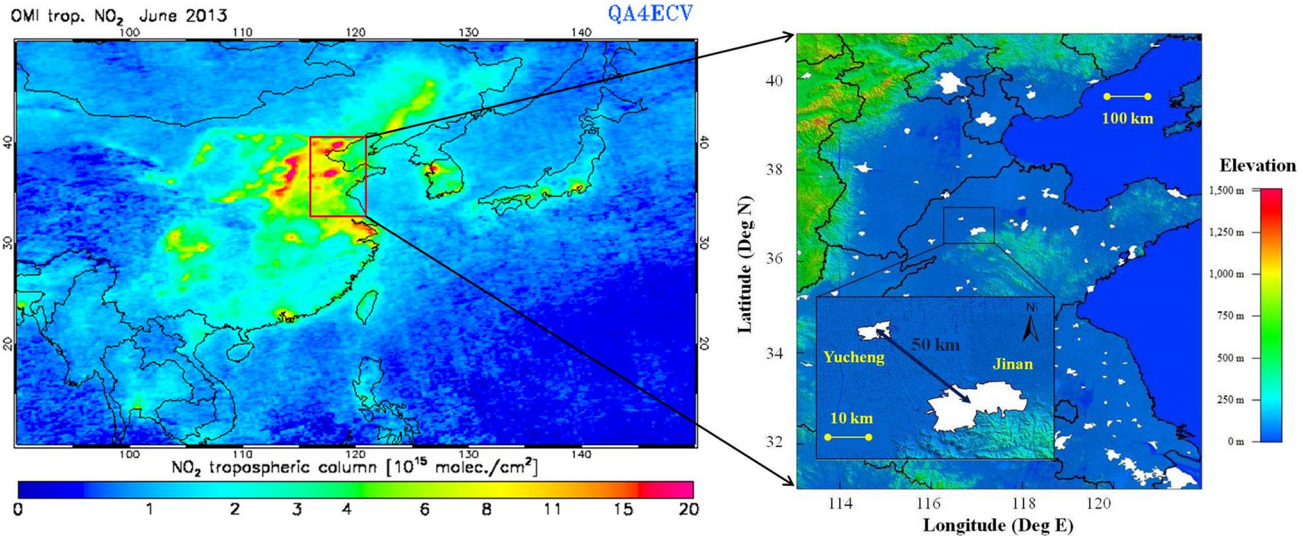

Fig. 1 – Left: Map showing the study area, color-coded by the OMI-derived monthly mean NO_2 column density in June 2013 (http://www.temis.nl/airpollution/no2.html). Right: Map showing the NCP region and study site. Note that urban and industrial areas are shown in white. NCP: North China Plain; NO_2: nitrogen dioxide.

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apply an observation-based model (OBM) to examine the ozone formation regimes. This study highlights the important combined effect of urban anthropogenic emission and rural biogenic sources on regional O_3 formation in the NCP, which may have general implications for understanding the causes of regional secondary pollution in China.

1. Methodology

1.1. Field observations

The field measurements were carried out from 1 June 2013 to 6 July 2013 in a rural area of Yucheng (36°52′ N, 116°34′ E) in Shandong province. Although Yucheng belongs to Dezhou city, it is located about 50 km northwest of Ji'nan, the capital city of Shandong province with a population of 7 million (see Fig. 1). As the prevailing winds in summer were from the south/southeast under the influence of the Asian monsoon (see Fig. 2), the study site is generally located in the downwind of Ji'nan and other upwind cities such as Tai'an and Ji'ning. A steel container that housed the measurement instruments was placed in an area of open farmland. There were few pollution sources within a 30 km radius of the site, except for a highway (G308) that is situated ~1.5 km to the south. Detailed descriptions of the study site have been provided elsewhere (Wen et al., 2015; Zhu et al., 2015).

O_3, O_3 precursors, related pollutants and meteorological parameters were measured by a set of techniques that have been widely used in many previous studies (*e.g.*, Xue et al., 2014a, 2014b). Briefly, O_3 was measured by a commercial ultraviolet absorption analyzer (*TEI model 49C*); CO with a non-dispersive infrared analyzer (*API model 300E*); SO_2 by a pulsed UV fluorescence analyzer (*TEI model 43C*); NO and NO_2 by a chemiluminescence analyzer with molybdenum oxide converter (*TEI model 42C*). Hydrocarbons were measured by taking whole air samples in 3.2 L stainless steel canisters followed by gas chromatograph separation plus flame ionization detection and mass spectrometry detection. It is noteworthy that the VOC sampling was only made during the latter period of the study, *i.e.*, after 28 June. In general, two samples were collected per day at 6:00 and 14:00 local time, while eight samples were taken every two hours from 6:00 to 20:00 on three selected episodes, *i.e.*, 28 June, 29 June and 6 July. A total of 45 VOC samples were taken during the measurement period. The VOC measurements have been reported by Zhu et al. (2015). Fifty-eight C_1–C_{10} hydrocarbon species were detected in the present study (Zhu et al., 2015). It should be noted that only the abundant hydrocarbon compounds were observed and some reactive VOC species such as carbonyls were not measured (though formation of secondary carbonyls can be taken into account to some extent in the MCM model). Thus part of the VOC reactivity may be missed from our observations. Meteorological parameters including temperature, relative humidity (RH), ultraviolet radiation (UV) and wind speed and direction were continuously recorded by an automatic weather station (*MILOS520, Vaisala, Finland*).

1.2. Observation-based model

The OBM-AOCP (Observation-Based Model for investigating Atmospheric Oxidative Capacity and Photochemistry) was utilized to elucidate the *in situ* O_3 production at Yucheng and its relationship with precursors. The model has been applied in several previous studies to dissect O_3 formation (Xue et al., 2014b) and RO_X radical chemistry (Xue et al., 2015, 2016), and

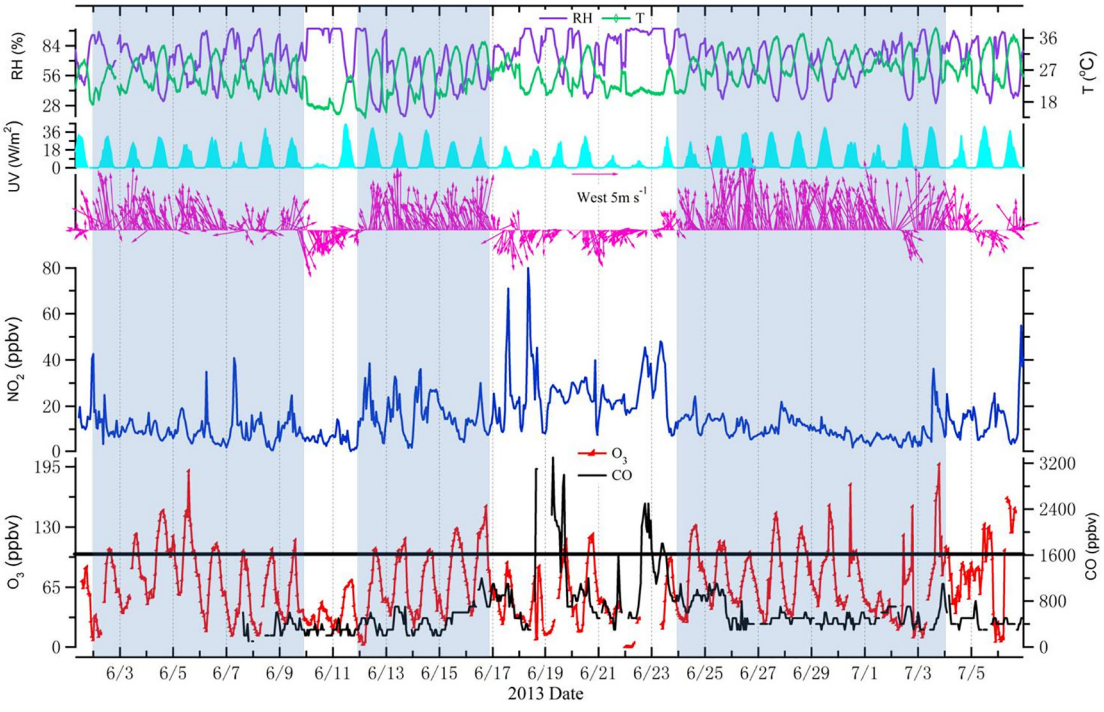

Fig. 2 – Time series of O_3, CO, NO_2 and meteorological parameters measured at Yucheng from 1 June to 6 July 2013.

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the chemistry has been updated in the present study to the latest version of the Master Chemical Mechanism, version 3.3.1 (Jenkin et al., 2003, 2015; Saunders et al., 2003). Dry deposition velocities for a variety of organic and inorganic gases were taken from Zhang et al. (2003). The boundary layer height (BLH) was assumed to vary from 300 m during the night to 1500 m in the afternoon (Xue et al., 2014b). The photochemical production, destruction and net rates of O_3 were simultaneously computed by the model. Detailed information about the model configuration and calculation of O_3 production rate has been described elsewhere (*e.g.*, Xue et al., 2014a, 2014b).

The model was constrained by the intensive set of observations to represent the measured real atmospheric conditions. The observed concentrations of O_3, CO, NO, SO_2, VOCs, temperature and RH were processed into the model inputs with a time resolution of 1 hr. For the VOCs for which the measurements were not in real-time, the daytime data in a time interval of 2 hr were interpolated to hourly resolutions, while the nighttime concentrations were assumed to be constant with the measured values at 20:00 local time. Our chemical box model was constrained these detailed hourly observational data to calculate the instantaneous ozone production, loss and net rates. In the present study, the model calculations were only performed for 28 and 29 June 2013, two ozone pollution episodes with intensive VOC measurements. The model calculation started from 00:00 local time and ended at 24:00 on each day. The model was run five times to stabilize the simulation of the unmeasured species, and the results of the final run were subject to formal analyses.

2. Results and discussion

2.1. Characteristics of ozone pollution

Fig. 2 shows the measured time series of O_3 pollution and meteorological conditions at Yucheng during the intensive study. The weather conditions consisted of relatively high temperatures (with average ± standard deviation of 26 ± 5°C), moderate relative humidity (70.6% ± 21.0%) and prevailing strong southerly winds. Severe photochemical air pollution coincided with the southerly/southeasterly winds, with the O_3 mixing ratios exceeding the national ambient air quality standards of China (Class II: ~75 and ~93 ppb for the 8-hr average and hourly values), indicative of the transport of urban plumes from the upwind cities (*e.g.*, Ji'nan, Tai'an and Ji'ning) to the study site. Three prolonged photochemical smog episodes were encountered during 2–9 June (eight days), 12–16 June (five days) and 24 June–3 July (ten days), when southerly/southeasterly winds persisted. Throughout the 36-day measurement period, 28 O_3 non-attainment days (a frequency of 78%) were recorded, with a maximum hourly O_3 value of 198 ppbv. Therefore, even this short investigation of measurement data clearly reveals the serious situation of summertime ozone pollution in the central NCP region.

Table 1 summarizes the ozone pollution situations observed in recent years in the major industrialized regions of China, *i.e.,* the NCP, Yangtze River Delta, Pearl River Delta and western China. It shows that all of these regions are suffering from regional O_3 pollution, which is as expected given their rapid economic development and increasing emissions of O_3 precursors in the past decades. Nevertheless, the ozone pollution in the NCP is much more serious than in the other regions, in terms of not only the extreme levels recorded but also the frequency of pollution episodes. In particular, the O_3 episode occurrence (78%) at Yucheng is among the highest ever reported in China. Overall, this comparison highlights the severity of the regional ozone problem in the NCP region, including the central part where previous investigations have been rare.

Fig. 3 shows the average diurnal profiles of O_3, related trace gases and meteorological parameters at Yucheng. This figure clearly illustrates the well-defined diurnal variations of O_3 pollution for this polluted rural environment. The O_3 mixing ratios were at a minimum (~34 ppbv) in the early morning (around 5:00 LT) and a broad peak (~102 ppbv) in the late afternoon (~16:00 LT). The late afternoon peak again suggests the transport of processed urban plumes from the upwind region, and the dramatic average daytime O_3 build-up (*i.e.*, 68 ppbv) indicates the strong regional ozone production in the study area. CO exhibited a similar diurnal pattern to ozone but with a gentle broad daytime concentration peak, indicating that the CO sources were regional. In comparison, NO_X showed a prominent morning peak with lower levels in the afternoon and at night, which is likely to be the combined result of evolutions in anthropogenic emissions, boundary layer height and chemical processing. Inspection of diurnal variations clearly indicates the influence of upwind urban plumes and strong regional photochemical ozone formation at Yucheng.

We also examined the hydrocarbon reactivity and distribution obtained at Yucheng (Fig. 4). To facilitate a VOC speciation analysis, the 58 species measured were categorized into biogenic hydrocarbons (BHC; including only isoprene in this study) and anthropogenic hydrocarbons (AHC), which were further grouped into alkenes, reactive aromatics (R-AROM; including all aromatics except benzene), alkanes with ≥4 carbons (C4HC), and less reactive hydrocarbons (LRHC; including ethane, propane, ethyne, benzene and acetonitrile). The OH reactivity was calculated individually for the VOC species, as the product of VOC concentration and the rate constant for the reaction with OH (Xue et al., 2014b). The total hydrocarbon reactivity for the study was 2.07 (± 0.15) sec^{-1} at Yucheng, which is much lower than those measured in the suburban areas downwind of Shanghai (5.85 sec^{-1}), Guangzhou (5.23 sec^{-1}) and Lanzhou (9.33 sec^{-1}) and at a rural site downwind of Beijing (2.77 sec^{-1}) (Xue et al., 2014b). This indicates that despite the elevated O_3 levels, the abundances of reactive VOCs are quite low at Yucheng, most probably due to the rarity of anthropogenic sources near the study site and the extensive chemical processing of regional plumes. Indeed, the air masses arriving at the Yucheng site were rather photochemically aged, as evidenced by the high ratios of ethylbenzene/m,p-xylenes (Zhu et al., 2015).

Isoprene was the most important reactive VOC compound at Yucheng and accounted for 53%, on average, of the hydrocarbon reactivity. For the reactive AHC, the most significant group was alkenes with a mean contribution of 18%, followed by reactive aromatics (14%) and C_4HC (12%). Fig. 5 presents the daytime profiles of AHC and BHC on two cases when multiple VOC samples were collected. Distinct diurnal variations of AHC and

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Table 1 – Comparison of the O_3 pollution conditions in major developed regions of China.

Regions	City/sites	Type	Period	O_3 pollution			References
				Hourly max (ppbv)	N. o. E. (days)	Percentage (%)	
North China Plain (NCP)	Yucheng	Rural	1 Jun–6 Jul 2013	198	28	78	This study
	Beijing	Rural	20 Jun–31 Jul 2005	286	18	44	Wang et al., 2006
	Tianjin	Suburban	Jul–Aug 2009	–	–	50	Ran et al., 2012
Yangtze river Delta (YRD)	Nanjing	Suburban	Jun 2012	268	3	10	Ding et al., 2013
			Jul 2012	237	3	10	
	Shanghai	Urban	5–31 Aug 2010	87	–	–	Li et al., 2012
	Jinshan	Suburban	Jul–Aug 2009	–	–	29	Ran et al., 2012
	Taicang	Rural	4 May–1 Jun 2005	127	6	21	Xue et al., 2014b
Pearl River Delta (PRD)	Hong Kong	Urban	1 Oct–31 Dec 2002	203	9	10	Zhang et al., 2007
	Guangzhou	Suburban	20 Apr–May 2004	178	7	19	Xue et al., 2014b
	Xinken	Rural	1 Oct–6 Nov 2004	160	–	76	Zhang et al., 2008
West China	Lanzhou	Suburban	19 Jun–16 Jul 2006	143	8	29	Xue et al., 2014b
	Xi'an	Urban	Mar 2008–Jan 2009	140	10	3	Wang et al., 2012

"N.o.E": the number of days with 1-hour average O_3 concentration exceeding the Class II NAAQS-China (*i.e.*, 93 ppbv).

BHC are noticeable from this figure. AHC shows higher mixing ratios in the early morning period which then decrease with time throughout the day as a result of photochemical processing. On the contrary, BHC presents a time-dependent increase with an afternoon concentration peak, which is due to the enhanced local biogenic emissions at higher temperatures. These results suggest the important role of biogenic VOCs in the *in situ* photochemical ozone production at Yucheng.

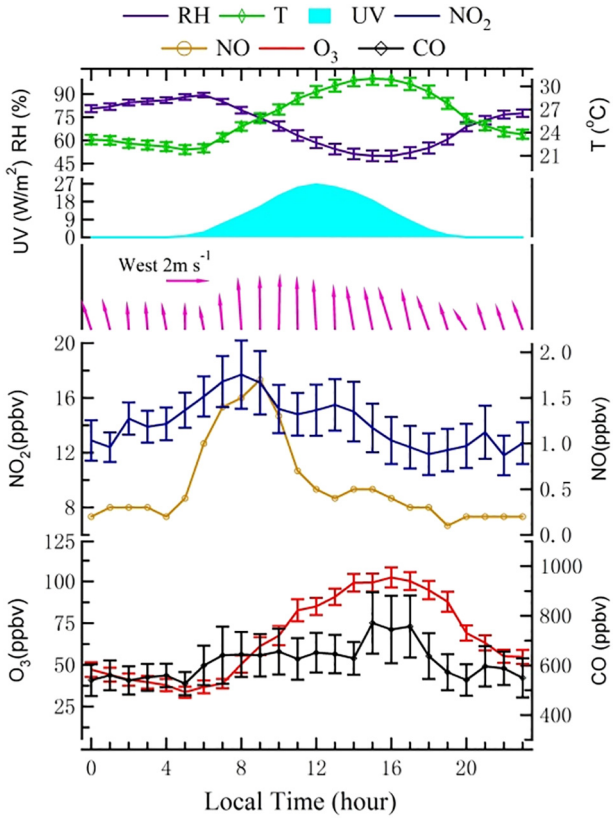

Fig. 3 – Average diurnal variations of O_3, CO, NO_2, NO and meteorological parameters at Yucheng in summer 2013. The error bars indicate the standard error of the mean. Note that the NO_2 measurements in the present study may be subject to positive interference from NOz species due to the molybdenum catalytic conversion method.

2.2. Contributions of urban plume and in situ photochemistry

The aforementioned analysis qualitatively revealed the effects of urban plume transport and *in situ* photochemical production on the observed ozone pollution at Yucheng. In this section, we further evaluate their contributions using detailed case studies. Fig. 5 depicts the time series measured on 28 and 29 June 2013,

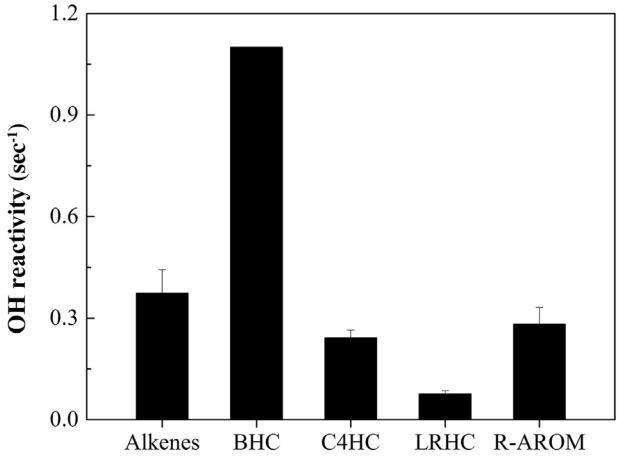

Fig. 4 – Average OH reactivity for major hydrocarbon groups for the study duration. BHC refers to biogenic hydrocarbons and contains only isoprene in the present study. C4HC refers to the alkanes with ≥4 carbon atoms; LRHC refers to the low-reactivity hydrocarbons and includes ethane, propane, ethyne, benzene and acetonitrile; R-AROM refers to the aromatic hydrocarbons expect for benzene. The error bars indicate the standard error of the mean. BHC: biogenic hydrocarbon; OH: biogenic hydrocarbon.

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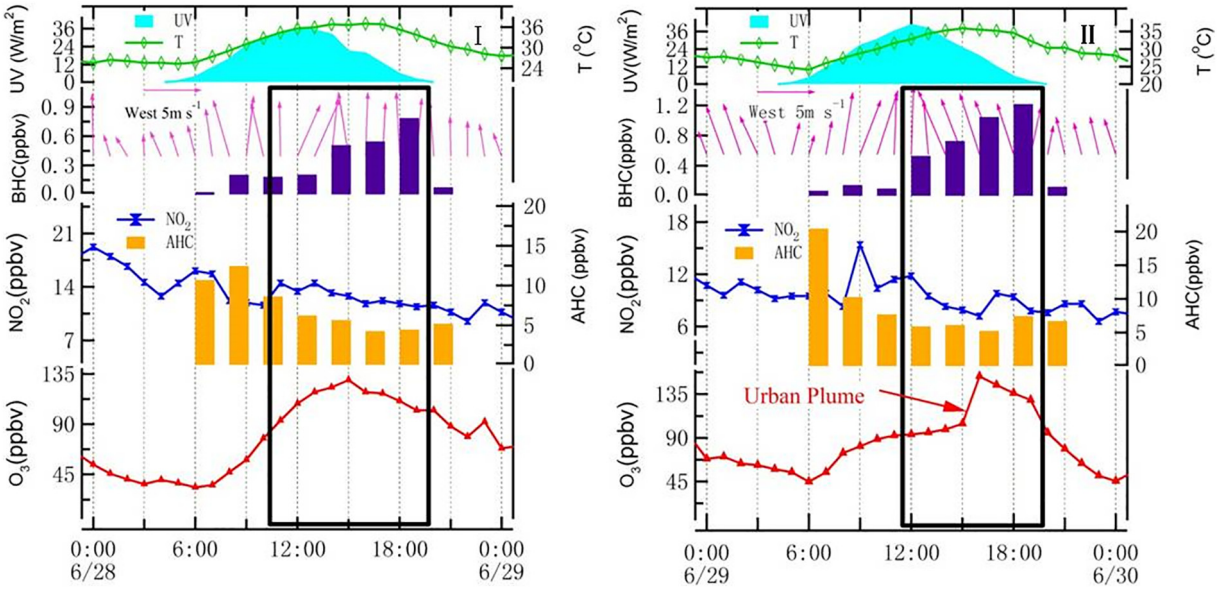

Fig. 5 – Times series of O_3 pollution and meteorological condition at Yucheng during two pollution episodes: (a) 28 June 2013 and (b) 29 June 2013.

two O_3 episodes with intensive VOC observations available. Rapid O_3 accumulation at daytime can be clearly observed from the figure. The O_3 build-up, calculated as the increment in O_3 concentrations from early morning to the O_3 maxima, was approximately 93 ppbv on 28 June and 110 ppbv on 29 June, demonstrating the intense photochemical formation over the region. Of much interest is the spike in O_3 values in the late afternoon of 29 June (*i.e.*, an increase of ~50 ppbv from 15:00 to 16:00 LT). Such a sharp increase is believed to be due to the transport of upwind O_3-laden urban plumes, given the weakened *in situ* photochemistry with relatively lower levels of NO_X and VOCs. We assessed the 24-hour backward trajectories by the Hybrid Single-Particle Lagrangian Integrated model (HYSPLIT, v4.9; Draxler and Rolph, 2016), and the results showed that the air masses passed over the upwind urban areas such as Ji'nan, Tai'an and Ji'ning prior to arriving at the Yucheng site (figures not shown here). Out of the 28 O_3 episode days, 15 (~54%) were marked by similarly sharp O_3 spikes in the late afternoon, highlighting the frequent export of urban plumes to the study site.

To further quantify the contributions of local formation and regional transport, the *in situ* O_3 production rate was predicted by the observation-based model. The model-computed O_3 production, destruction and net rates are presented in Fig. 6. The daytime average (07:00–18:00 LT) net O_3 production rates were calculated as 3.9 and 4.8 ppb/hr for each episode, respectively. Such levels are of the same magnitude as the modeled rates at a rural site downwind of Beijing (5.8 ppb/hr; Xue et al., 2014b) and Mt. Tai (6.4 ppb/hr; Kanaya et al., 2009) in the NCP region, but are much lower than those obtained at suburbs downwind of Shanghai and Guangzhou (25 and 30 ppb/hr; Xue et al., 2014b). This is as expected due to the lower abundance of O_3 precursors at Yucheng. The locally produced amounts of O_3, as estimated by integrating the *in situ* production rates from early morning to the O_3 maximum, were 43 and 51 ppbv during the two episodes, which could only explain 46.2% and 46.4% of the observed O_3 accumulation. As such, about 54% of the O_3 pollution observed at Yucheng is attributable to the regional transport of urban plume from the upwind urban areas.

Fig. 6 also shows the breakdown of the ozone production and loss pathways simulated at Yucheng. Overall, the O_3 production is dominated by the oxidation of NO by HO_2 which accounts for 63% and 57% of the total in both cases, and the remaining (37% and 43%) is contributed by the NO oxidation by RO_2. For the O_3 loss, the major pathway is the O_3 photolysis, with average contributions of 36% and 33%, followed by the reactions of $O_3 + HO_2$ (25% and 26%) and $OH + NO_2$ (16% and 13%). Note that NO_2 was not constrained but simulated in the model, thus the estimation of contributions of $OH + NO_2$ reactions may be subject some uncertainties.

2.3. Ozone formation regime

The *in situ* O_3 formation regimes were further assessed by conducting a set of sensitivity model simulations with assumed reductions in different O_3 precursors. Relative incremental reactivity (RIR), defined as the percentage decrease in the net ozone production rates per decrease of target precursors (Cardelino and Chameides, 1995), is a useful indicator to infer the O_3 formation regimes and has been applied in many previous studies (*e.g.*, Cheng et al., 2010; Kanaya et al., 2009; Lyu et al., 2015; Xue et al., 2014b; Zhang et al., 2007). Note that such OBM-estimated O_3 formation regimes are only relevant for the *in situ* produced O_3 at the study site, but not for the regional O_3 produced during the transport of urban plumes. The model-calculated RIRs for the individual major O_3 precursors and the VOC sub-groups at Yucheng are documented in Fig. 7. The results obtained for the two episodes are quite similar. NO_X, CO and VOCs all show positive RIR values (see Fig. 7a and b), indicating that the O_3 formation at Yucheng was in a transition regime that the *in situ* O_3 production was limited by all its precursors. Such a transition chemical regime means a much

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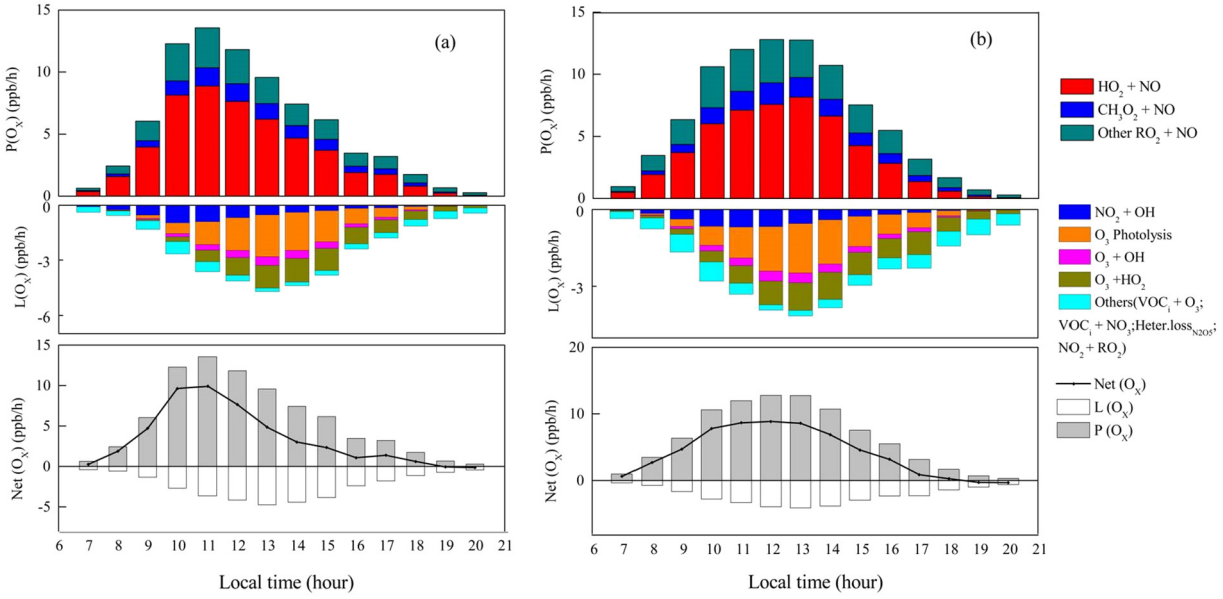

Fig. 6 – The OBM-simulated *in situ* O_3 production, destruction and net rates and their breakdown at Yucheng on (a) 28 June 2013 and (b) 29 June 2013. OBM: observation-based model; O_3: ozone.

flexible O_3 pollution control strategy since either reducing NOx or VOCs emissions could efficiently mitigate local O_3 production. This is similar to the results obtained at a rural site to the north of Beijing downtown and at a suburban site in Lanzhou, but is different from the results obtained from urban and suburban sites in Shanghai, Guangzhou and Hong Kong, where VOCs-controlled O_3 formation regime was determined (Xue et al., 2014a, 2014b). In general, the O_3 production is commonly in a VOCs-controlled regime in polluted urban and suburban areas, compared to transition or NOx-limited regimes in relatively clean rural and remote regions (Wang et al., 2017).

With regard to the specific VOC groups, both AHC and BHC show the comparable RIR values (*i.e.*, 0.29–0.30 for AHC and 0.26–0.31 for BHC) on both episodes (Fig. 7a and b), demonstrating the important contributions of both anthropogenic and biogenic VOCs in controlling the *in situ* O_3 production at Yucheng. If we further examine the RIR for individual VOC sub-groups, the BHC clearly showed the highest RIR values (Fig. 7c and d), elucidating the significant role of BVOCs in the local O_3 formation at Yucheng. Note that only isoprene as a biogenic VOC was detected in the present study. Based on the vegetation type in the study area (mainly corn and wheat) and the emission ratios of monoterpenes/isoprene from the literature (Kinnee et al., 1997), we roughly estimated the mixing ratios of monoterpenes (*i.e.*, α/β-pinenes) from the measured isoprene levels. Sensitivity modeling analysis including monoterpenes suggested that the contributions of BVOCs to local ozone formation were dominated by isoprene. In terms of anthropogenic VOCs, alkenes showed the highest RIR values (0.14 and 0.10), whilst reactive aromatics, C4HC and LRHC showed relatively smaller RIR values (<0.03). This is different from the results obtained from the suburban areas downwind of Guangzhou and Shanghai, where the O_3 formation was the most sensitive to aromatics and both aromatics and alkenes (Xue et al., 2014b).

It is noteworthy that the NO_2 observations were made in the present study by the traditional approach deploying molybdenum oxide (MoO) conversion of NO_2 to NO followed by chemiluminescence detection. Xu et al. (2013) evaluated the performance of several commonly-used NO_2 measurement techniques and found that such traditional methods may significantly overestimate in the polluted rural atmospheres. Considering the uncertainty of our NO_2 measurements, the OBM was not constrained by the observed NO_2 data. With constraints of the measured NO and O_3 data, together with the model simulated radicals, the model should work reasonably well to predict the NO_2 concentrations. Nevertheless, it should be noted that the present modeling results may be subject some uncertainty from the above treatment.

The present study provides solid evidence that the transport of polluted urban plumes combines with *in situ* photochemical production to cause the severe O_3 pollution in rural areas of the NCP region. The ozone production at Yucheng was in a transition regime, and controlling NOx and VOCs would be effective for reducing O_3 pollution. In particular, the local emissions of biogenic VOCs played an important role in the O_3 formation in the rural area. Although the modeling analyses were only conducted for two episodes due to the limitation of VOC observations, these cases were quite typical for the O_3 pollution episodes during the whole measurement period. As shown in Fig. 2, 20 O_3 episodes (out of the total of 28) were featured by similar meteorological conditions (especially the southerly or southeasterly winds) and comparable O_3 precursors to 28 and 29 June. Furthermore, the NCP region is home to numerous urban and industrial areas with intense anthropogenic emissions, which are surrounded by the vast farmlands, as the case of the study area in this work. Therefore, the research results obtained from the present study should have some general applicability for the regional ozone pollution in the NCP region. In past decades, rapid urbanization in eastern China has created a

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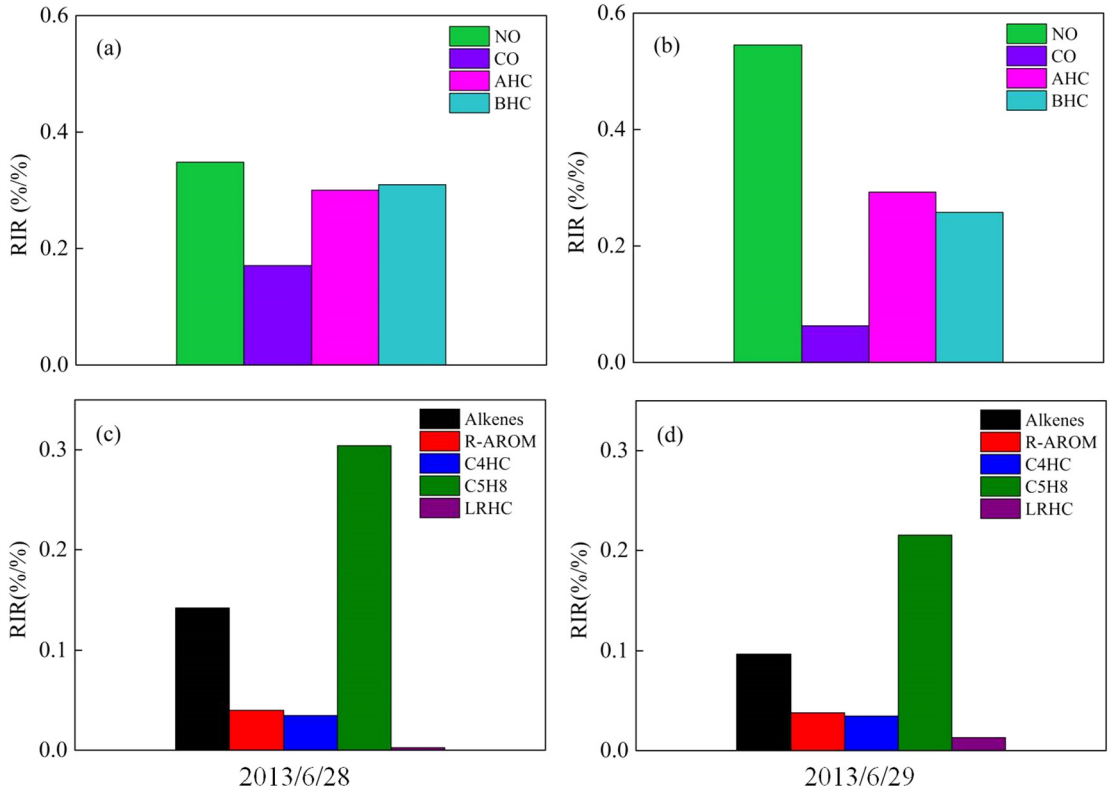

Fig. 7 – The OBM-calculated RIR for major O_3 precursors and the VOC sub-groups for (a) and (c) 28 June, (b) and (d) 29 June. The upper panel shows the RIRs for NO_X, CO, AHC and BHC; the bottom panel shows the RIRs for the VOC sub-groups including alkenes, R-AROM, C4HC, isoprene and LRHC. OBM: observation-based model; O_3: ozone; VOC: volatile organic compound; BHC: biogenic hydrocarbon; RIR: relative incremental reactivity; LRHC: low-reactivity hydrocarbon; R-AROM: reactive aromatics; C4HC: alkanes with ≥4 carbons.

number of pollution "hotspots" (*i.e.*, large cities) in a region of vast rural areas with extensive biogenic VOC sources. It has also been found that the regional air pollution, marked by unhealthily high levels of O_3 and fine particles, is now widespread and continues to worsen over eastern China (*e.g.*, Ding et al., 2013; Xue et al., 2014b; Zhang et al., 2014, 2008; Zhao et al., 2009). The pollution formation mode as unraveled in this study, which combines the effects of both anthropogenic pollution from urban zones and biogenic emissions in rural areas, may also act in the other areas of eastern China. It is therefore helpful for better understanding the formation of regional secondary air pollution (including ozone and secondary aerosols) in China.

3. Summary

We report our recent intensive measurements focusing on ozone pollution at a polluted rural site in the central NCP region during summer 2013. The highest frequency by far (78%, or 28 out of 36 days) of the non-attainment O_3 episodes and the hourly O_3 maximum of 198 ppbv demonstrates the serious situation of regional O_3 pollution in the NCP. Examinations of diurnal variations and day-by-day case studies illustrate the extensive transport of polluted plumes from the upwind urban areas to the study site. The VOC reactivity was relatively low and dominated by isoprene as a result of the intense local biogenic emissions. The *in situ* O_3 photochemical formation was quantified by an observation-based box model for two episodes. The moderate *in situ* production accounted for ~46% of the observed O_3 accumulation at daytime, while regional transport of well-processed urban plume contributed to the remaining ~54%. Sensitivity modeling studies indicate that the O_3 formation at Yucheng was in a mixed controlled regime, indicating reducing either NOx or VOCs could result in a reduction in local ozone formation. Biogenic VOCs played a significant role in O_3 formation. Therefore, export of anthropogenic pollution from urban areas coupling with the biogenic VOC-induced *in situ* photochemistry is the cause of the severe O_3 pollution in rural atmospheres of the NCP and other polluted regions of China. Both urban emission and rural biogenic sources need to be taken into account to establish an effective control strategy for regional secondary air pollution in China.

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