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

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ARTICLE INFO

Article history:
Received 24 December 2017
Revised 28 April 2018
Accepted 5 May 2018
Available online xxxx

Keywords:
Ozone
Regional transport
In situ photochemical formation
Biogenic VOCs
Observation-based model
North China Plain

ABSTRACT

Regional ozone (O₃) 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 O₃ problem in the North China Plain (NCP), intensive field measurements of O₃ 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 O₃ pollution was recorded, with the O₃ 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 O₃ production on two episodes. The results show that the in situ formation accounted for approximately 46% of the observed O₃ accumulation, while the remainder (~54%) was contributed by regional transport of the O₃-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 O₃ 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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https://doi.org/10.1016/j.jes.2018.05.003
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Please cite this article as: Zong, R., et al., Strong ozone production at a rural site in the North China Plain: Mixed effects of urban plumes and biogenic emissions, J. Environ. Sci. (2018), https://doi.org/10.1016/j.jes.2018.05.003
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 (NOX = 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., NOX 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 NOX 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.
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 O₃ 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).

O₃, O₃ 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, O₃ was measured by a commercial ultraviolet absorption analyzer (TEI model 49C); CO with a non-dispersive infrared analyzer (API model 300E); SO₂ by a pulsed UV fluorescence analyzer (TEI model 43C); NO and NO₂ 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 C₁–C₁₀ 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 Atmospheic Oxidative Capacity and Photochemistry) was utilized to elucidate the in situ O₃ production at Yucheng and its relationship with precursors. The model has been applied in several previous studies to dissect O₃ formation (Xue et al., 2014b) and ROX radical chemistry (Xue et al., 2015, 2016), and

![Fig. 2 – Time series of O₃, CO, NO₂ and meteorological parameters measured at Yucheng from 1 June to 6 July 2013.](image-url)
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 O₃ were simultaneously computed by the model. Detailed information about the model configuration and calculation of O₃ 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 O₃, CO, NO, SO₂, 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 O₃ 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 O₃ 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., Jin’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 O₃ non-attainment days (a frequency of 78%) were recorded, with a maximum hourly O₃ 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 O₃ pollution, which is as expected given their rapid economic development and increasing emissions of O₃ 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 O₃ 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 O₃, related trace gases and meteorological parameters at Yucheng. This figure clearly illustrates the well-defined diurnal variations of O₃ pollution for this polluted rural environment. The O₃ 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 O₃ 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, NOₓ 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, ethylene, 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 O₃ 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-xylene (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 C₄HC (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
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.

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, with...
two O₃ accumulation with intensive VOC observations available. Rapid O₃ accumulation at daytime can be clearly observed from the figure. The O₃ build-up, calculated as the increment in O₃ concentrations from early morning to the O₃ 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 O₃ 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 O₃-laden urban plumes, given the weakened in situ photochemistry with relatively lower levels of NO₂ 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 Jīn’ān, Tai’ān and Ji’ning prior to arriving at the Yucheng site (figures not shown here). Out of the 28 O₃ episode days, 15 (~54%) were marked by similarly sharp O₃ 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 O₃ production rate was predicted by the observation-based model. The model-computed O₃ production, destruction and net rates are presented in Fig. 6. The daytime average (07:00 – 18:00 LT) net O₃ 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 O₃ precursors at Yucheng. The locally produced amounts of O₃, as estimated by integrating the in situ production rates from early morning to the O₃ maximum, were 43 and 51 ppbv during the two episodes, which could only explain 46.2% and 46.4% of the observed O₃ accumulation. As such, about 54% of the O₃ 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 O₃ production is dominated by the oxidation of NO by HO₂ 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 RO₂. For the O₃ loss, the major pathway is the O₃ photolysis, with average contributions of 36% and 33%, followed by the reactions of O₃ + HO₂ (25% and 26%) and OH + NO₂ (16% and 13%). Note that NO₂ was not constrained but simulated in the model, thus the estimation of contributions of OH + NO₂ reactions may be subject some uncertainties.

2.3. Ozone formation regime

The in situ O₃ formation regimes were further assessed by conducting a set of sensitivity model simulations with assumed reductions in different O₃ 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 O₃ 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 O₃ formation regimes are only relevant for the in situ produced O₃ at the study site, but not for the regional O₃ produced during the transport of urban plumes. The model-calculated RIRs for the individual major O₃ precursors and the VOC sub-groups at Yucheng are documented in Fig. 7. The results obtained for the two episodes are quite similar. NOₓ, CO and VOCs all show positive RIR values (see Fig. 7a and b), indicating that the O₃ formation at Yucheng was in a transition regime that the in situ O₃ production was limited by all its precursors. Such a transition chemical regime means a much
flexible O₃ pollution control strategy since either reducing NOx or VOCs emissions could efficiently mitigate local O₃ 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 O₃ formation regime was determined (Xue et al., 2014a, 2014b). In general, the O₃ 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 O₃ 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 O₃ 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/isoprene from the literature. 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 O₃ formation was the most sensitive to aromatics and both aromatics and alkenes (Xue et al., 2014b).

It is noteworthy that the NO₂ observations were made in the present study by the traditional approach deploying molybdenum oxide (MoO) conversion of NO₂ to NO followed by chemiluminescence detection. Xu et al. (2013) evaluated the performance of several commonly-used NO₂ measurement techniques and found that such traditional methods may significantly overestimate in the polluted rural atmospheres. Considering the uncertainty of our NO₂ measurements, the OBM was not constrained by the observed NO₂ data. With constraints of the measured NO and O₃ data, together with the model simulated radicals, the model should work reasonably well to predict the NO₂ 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 O₃ 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 O₃ pollution. In particular, the local emissions of biogenic VOCs played an important role in the O₃ 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 O₃ pollution episodes during the whole measurement period. As shown in Fig. 2, 20 O₃ episodes (out of the total of 28) were featured by similar meteorological conditions (especially the southerly or southeasterly winds) and comparable O₃ 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
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 O₃ 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 O₃ episodes and the hourly O₃ maximum of 198 ppbv demonstrates the serious situation of regional O₃ 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 O₃ photochemical formation was quantified by an observation-based box model for two episodes. The moderate in situ production accounted for ~46% of the observed O₃ accumulation at daytime, while regional transport of well-processed urban plume contributed to the remaining ~54%. Sensitivity modeling studies indicate that the O₃ 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 O₃ formation. Therefore, export of anthropogenic pollution from urban areas coupling with the biogenic VOC-induced in situ photochemistry is the cause of the severe O₃ 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.

Acknowledgements

The field measurements in the present study were funded by the Taishan Scholar Grand (No. ts20120552) and the National Natural Science Foundation of China (No. 41375126). The data analyses and modeling studies are supported by the National Natural Science Foundation of China (No. 41675118), the Qilu
Youth Talent Programme of Shandong University, and the Jiangsu Collaborative Innovation Center for Climate Change.

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