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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

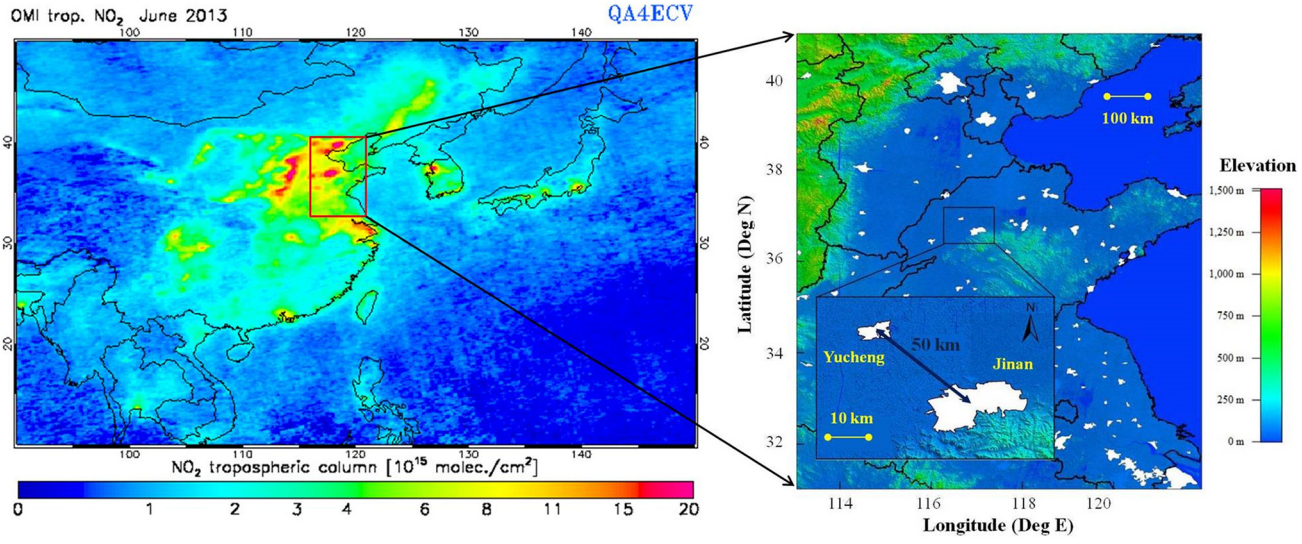

Fig. 1 – Left: Map showing the study area, color-coded by the OMI-derived monthly mean NO_2 column density in June 2013 (http://www.temis.nl/airpollution/no2.html). Right: Map showing the NCP region and study site. Note that urban and industrial areas are shown in white. NCP: North China Plain; NO_2: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

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