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Differences in ozone photochemical characteristics between the megacity Tianjin and its rural surroundings

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HIGHLIGHTS

- Ozone and its precursors were measured in urban and rural areas in Tianjin.
- Difference in ozone and its precursors over time in urban and rural were analyzed.
- Differences in ozone photochemical oxidant production in urban and rural were analyzed.
- The sensitivity of O_3 concentrations to various NO_x and VOC conditions were analyzed.

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ABSTRACT

Ground level ozone and its precursors were measured from July 10 to September 30, 2009 within Tianjin. The data were used to analyze differences in ozone photochemical oxidant production in urban and rural areas. Results showed more pronounced risk of O_3 exposure at the rural site, Wuqing. During the observation period, ozone varied monthly, peaking in Jul. and reaching a minimum in Sep. The daily maximum ozone concentration was found to exceed 80 ppb for 28 days 100 ppb for 12 days, 120 ppb for 7 days at Wuqing, while it exceeded 80 ppb for 10 days, 100 ppb for 2 days, and 120 ppb for 1 day at the urban site, Tieta. The daily maximum ozone concentrations at Wuqing and Tieta were 193.7 ppb and 130.4 ppb. The daily maximum ozone concentration occurred at noon in Tieta and at 14:00 in Wuqing. NO and NO_x peaked in September and reached minimum values in Jul., CO showed little variation at both sites. NO_x and CO showed similar double-peak diurnal cycles resulted from a combination of diurnal variation of emission and the Planetary Boundary Layer During the VOCs (volatile organic compounds) sampling period, the average total VOCs concentration showed considerable day to day variation, which was 87.91 ppb with a range of 27.2 ppb–437.3 ppb at Tieta, and the average total VOCs was 197.95 ppb with a range of 63.48 ppb–473.97 ppb at Wuqing. A sensitivity study performed with the NCAR-MM model showed alkenes to be the most numerous contributors to O_3 production, accounting for 53.3% of the total. Aromatics and alkanes accounted for 35.1% and 9.2%, respectively.

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1. Introduction

Rapid urbanization and industrialization have led to a substantial degradation of air quality in some cities of China. In some megacities, severe ozone problems have become one of the most important air quality issues (Civeroloa et al., 2007; Lei et al., 2007; Tie et al., 2007, 2010; Stephens et al., 2008; Ying et al., 2009). Nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs) are the main precursors of ozone (O_3). The atmospheric oxidization has an important impact on formation of secondary aerosol.

Tianjin is a megacity in northern China. It has a population of over 12 million, more than 1.5 million automobiles, and an industrialized area, Binhai Industrial Area which is about 50 km east of the urban center. As industrial activity and the number of automobiles increase, the emissions of VOCs and NO_x ($NO + NO_2$) also increase significantly. Tianjin will probably continue to expand in response to ongoing economic growth, which may have a widespread and profound effect on air quality, which may not be limited to the city itself. Both VOCs and NO_x play critical roles in O_3

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formation (Sillman, 1995). Variations in their concentrations and the ensuing effects on the rate of O_3 production can be characterized as either NO_x-sensitive or VOCs-sensitive (Tang et al., 2008). Knowledge of the ozone photochemical production in Tianjin and its rural areas is therefore crucial to effective ozone control strategies.

Ambient ozone concentration is nonlinear with respect to many factors, such as the distribution of emissions, photochemical processes, transportation, and meteorological conditions (Qin et al., 2004; Geng et al., 2006; Jenkin and Clemitshaw., 2000; Jiang and Fast, 2004; Murphy and Allen, 2005; Tie et al., 2009). Concerns regarding ozone pollution have been addressed in many other megacities in China (Geng et al., 2008; Ran et al., 2009; Shao et al., 2005; Xie et al., 2009; Zhang et al., 2008). However, only a few studies have been performed on Tianjin (Bian et al., 2007; Han et al., 2009, 2011; Yue et al., 2009). The concentration of ozone and its photochemical precursors have not been measured systemically. Differences in ozone photochemical production between Tianjin and nearby rural areas are still not known. In the present paper, variations and difference in ozone and its precursors over time and between an urban and rural site are analyzed.

This paper is organized as follows. In Section 2, the methods used in this study, including instruments and measurements, are described. In Section 3, the measured results are analyzed with respect to the characterizations and differences in ozone and its precursors in Tianjin and nearby rural areas. The weekend effects of wind on ozone concentrations are analyzed.

2. Data and methods

2.1. Site description

Measurements of ground level ozone, NO, NO_x, and CO concentrations were performed every day between July 10 and September 30, 2009 at Wuqing Meteorological Station and Tieta Meteorological Station in Tianjin (Fig. 1). The urban monitoring site (Tieta) was located in an open area with an elevation of about 3 m above sea level. It was located at 39°06′N, 117°10′E. Within a radius of about 1 km of the measured area, the land was flat with some low residential buildings and many commercial buildings that steadily increased in density to the west and south. Heiniucheng road runs E–W at a mean distance of approximately 100 m from the monitoring site. Youyinan road extends S–N about 100 m east of the site. The rural site was located at a meteorological station in Wuqing at 39°23′N, 117°01′E, which was northwest of the town of Wuqing, about 80 km southeast of the megacity Beijing and 30 km northwest of Tianjin. There were no large sources of emissions near the Wuqing observation site. Traffic flow was lower than at the urban site (Tieta station).

2.2. Gas measurement

Ground level ozone, NO, NO_2, and CO concentrations were continuously measured using calibrated instruments from Thermo Environmental Instruments (U.S.). Values were reported as volume mixing ratios (ppb). A UV absorption ozone analyzer (EC9810B) consistent with technical requirements of the USEPA was used to measure ambient ozone concentrations. NO and NO_2 were measured continuously with an EC9841B. Nitrogen Oxide Analyzer using chemiluminescence technique. CO was observed using an EC9830B carbon monoxide analyzer.

Sampling of VOCs was conducted simultaneously at two sites with a sampling protocol. Five periods, 7:30–9:30, 11:30–13:00, 14:00–16:00, 17:00–19:00 and 21:00–23:00 were evaluated from evening on Aug 6 to midday on August 13, 2009. Analysis was performed in the laboratory after data was collected using USEPA methods TO-14A and TO-15. Air samples were analyzed using a GC/MS system. The VOCs were expressed as carbon atom-based concentrations with ppb. The detailed analytical method used to collect VOCs data were described by Lu et al. (2011).

2.3. Meteorological data

Meteorological data were observed at the Automatic Weather Station at the Wuqing meteorological station. Wind parameters were observed at 10 m off the ground. Temperature, pressure, and moisture were observed at a height of 1.5 m.

2.4. Data analysis

One-minute average ozone, NO, NO_x, and CO data were used to calculate 1-h averages when the missing data comprised less than

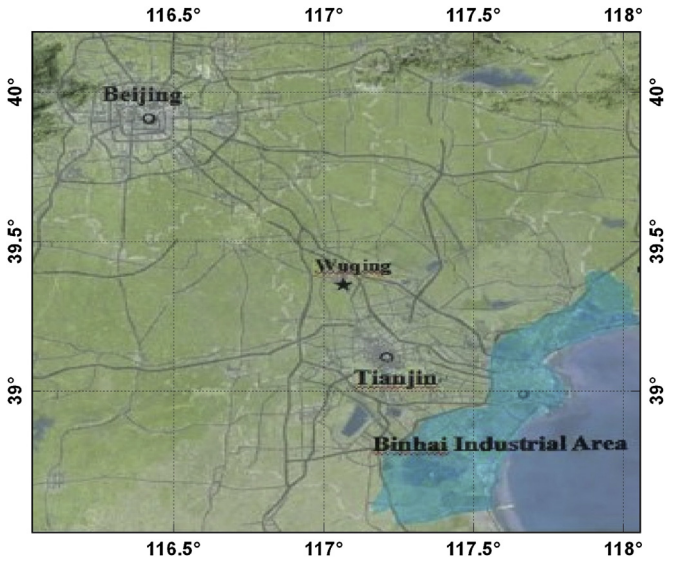

Fig. 1. Site.

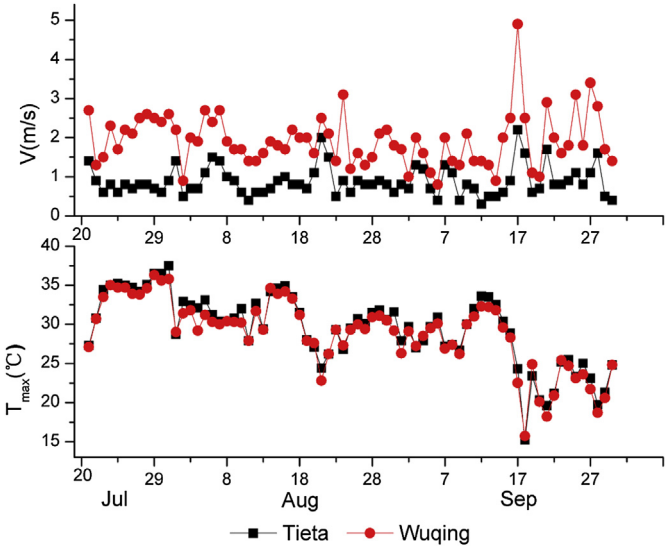

Fig. 2. Diurnal variation in wind speed and daily maximum temperature (T_{max}) at urban and rural sites from July to September.

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