Surface Trace Gases at a Rural Site between the Megacities of Beijing and Tianjin

RAN Liang¹, LIN Wei-Li², WANG Pu-Cai¹, and DENG Zhao-Ze¹

¹ Key Laboratory of Middle Atmosphere and Global Environment Observation, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China
² Centre for Atmosphere Watch and Services, Meteorological Observation Centre, China Meteorological Administration, Beijing 100081, China

Received 2 January 2014; revised 2 February 2014; accepted 19 February 2014; published 16 May 2014

Abstract The North China Plain (NCP) has recently faced serious air quality problems as a result of enhanced gas pollutant emissions due to the process of urbanization and rapid economic growth. To explore regional air pollution in the NCP, measurements of surface ozone (O₃), nitrogen oxides (NOₓ), and sulfur dioxide (SO₂) were carried out from May to November 2013 at a rural site (Xianghe) between the twin megacities of Beijing and Tianjin. The highest hourly ozone average was close to 240 ppbv in May, followed by around 160 ppbv in June and July. High ozone episodes were more notable than in 2005 and were mainly associated with air parcels from the city cluster in the hinterland of the polluted NCP to the southwest of the site. For NOₓ, an important ozone precursor, the concentrations ranged from several ppbv to nearly 180 ppbv in the summer and over 400 ppbv in the fall. The occurrence of high NOₓ concentrations under calm conditions indicated that local emissions were dominant in Xianghe. The double-peak diurnal pattern found in NOₓ concentrations and NO/NOₓ ratios was probably shaped by local emissions, photochemical removal, and dilution resulting from diurnal variations of surface wind speed and the boundary layer height. A pronounced SO₂ daytime peak was noted and attributed to downward mixing from an SO₂-rich layer above, while the SO₂-polluted air mass transported from possible emission sources, which differed between the non-heating (September and October) and heating (November) periods, was thought to be responsible for night-time high concentrations.

Keywords: ozone, nitrogen oxides, sulfur dioxide, North China Plain


1 Introduction

Trace gases such as sulfur dioxide (SO₂) and nitrogen oxides (NOₓ = NO + NO₂) primarily come from anthropogenic emissions in populated regions. SO₂ is largely emitted from coal combustion in power plants and domestic heating facilities, thus it serves as a reliable anthropogenic pollution indicator. SO₂ could play an important role in aerosol formation and acid precipitation, which have also long been environmental concerns (Seinfeld and Pandis, 1998). NOₓ is short-lived and mainly released from motor vehicles, power generation, and industrial processes. In addition, NOₓ is a critical precursor of the secondary gas pollutant ozone (O₃). In the presence of sunlight, O₃ is produced via a chain of photochemical reactions involving NOₓ and volatile organic compounds (Haagen-Smit et al., 1953). A high concentration of O₃ is detrimental to human health and vegetation (National Research Council, 1991; Chameides et al., 1994). The ozone problem has become a prevalent and complex environmental issue in the world (e.g., Chan and Yao, 2008; Stephens et al., 2008; Ran et al., 2009; Mao et al., 2010).

In the past decades, economic growth and urbanization has fostered the development of a cluster of cities including two megacities, Beijing and Tianjin, in the North China Plain (NCP). Due to the significant increase in the anthropogenic emissions of primary gaseous pollutants (Streets and Waldhoff, 2000; Van der A et al., 2008), the NCP has become one of the most polluted regions in the world (e.g., Shao et al., 2006; Lin et al., 2011). To better understand the impacts of city clusters and megacities on regional air pollution in the NCP, observations of gas pollutants at rural sites sitting in the city cluster would be insightful. Fingerprints of regional pollution and regional transport have been observed at a few rural and suburban sites (Wang et al., 2006; Ma et al., 2007; Lin et al., 2009; Xu et al., 2011a, b; Ge et al., 2012; Ran et al., 2012). High concentrations of gas pollutants were found to be usually associated with winds from the southwest-south sector. In this paper, we describe the characteristics of surface trace gases, including SO₂, NOₓ, and O₃, measured during May and November 2013 at a rural site, Xianghe, between the megacities of Beijing and Tianjin. Possible factors contributing to the observed seasonal and diurnal variations of these trace gases are analyzed and discussed.

2 Measurements

2.1 The site

The Xianghe station (39.80°N, 116.96°E) is a rural site
located in a small town in Hebei Province and operated by the Institute of Atmospheric Physics, Chinese Academy of Sciences. As shown in Fig. 1, the site lies about 45 km east-southeast of the megacity of Beijing and 70 km north-northwest of the megacity of Tianjin. To the southwest of the site there is a cluster of cities and towns, among which is a large city and industrial center with a population of over four million, Langfang, which is only about 30 km away. The site is in a well-vegetated and sparsely populated area, approximately 4 km to the west of the town center. The town of Xianghe is a transportation hub in the NCP, with an indigenous population of 330000 and more than 300000 migrants, with four railways, six highways, and four national roads surrounding or passing across the area. The mainstay industry in Xianghe is furniture manufacturing.

2.2 Instruments

O₃ and NOₓ were measured from May to November 2013. The lack of O₃ data in August and November was due to the malfunction of the instrument. SO₂ was measured during September and November. All the instruments were set up in an air-conditioned room using one inlet about 5 m above the ground. Ambient concentrations of O₃ were measured by a non-dispersive ultraviolet (UV) photometer (EC9810B, ECOTECH, Australia), meeting the technical requirements of the USA Environmental Protection Agency (USEPA). The oxides of nitrogen analyzer (EC9841B, ECOTECH) was used to simultaneously quantify NO and NOₓ using a heated molybdenum NO₂ to NO converter and the chemiluminescence technique. Surface SO₂ was monitored by a pulsed UV fluorescence analyzer (EC9850B, ECOTECH). Multipoint calibrations were performed every two months using a dynamic gas calibrator (Gascal 1100, ECOTECH) and the standard reference gas mixture (NO/CO/SO₂ in N₂), following USEPA recommendations on quality assurance and quality control (USEPA, 2008). The ozone analyzer was calibrated using the TE 49CPS calibrator. All trace gases were recorded as one-minute averages (mixing ratios by volume, ppbv). Meteorological parameters such as wind speed and wind direction were obtained from the automatic weather station installed at the site.

3 Results

3.1 Nitrogen oxides

Nitrogen oxides are relevant not only as primary gas pollutants, but also as an important ozone precursor. During the observational period, hourly NOₓ averages ranged from several ppbv to nearly 180 ppbv in the summer and over 400 ppbv in the fall. Figures 2a and 2b display the average diurnal variation of NO/NOₓ ratios and NOₓ concentrations for each month. Generally, there was a valley in the NOₓ concentrations and NO/NOₓ ratios in the day and higher values were observed at night. NOₓ concentrations averaged about 20 ppbv during the day and 30 ppbv at night in the summer, with a NO/NOₓ ratio between 10% and 30%. In the fall, NOₓ concentrations and NO/NOₓ ratios greatly increased, especially when the heating season began in November. Average NOₓ concentrations during the day were 30, 45, and 50 ppbv in September, October, and November, respectively. NO was found to account for about 20%, 26%, and 28% of the observed NOₓ concentrations in September, October, and November, respectively. At night, the average NOₓ concentrations increased to 50 ppbv in September, 90 ppbv in October, and 120 ppbv in November, with a NO/NOₓ ratio of around 50%.

The analysis of NOₓ and winds followed the methodology in Xu et al. (2011b) and revealed no apparent wind direction dependence of NOₓ concentrations (Fig. 3a). Generally, NOₓ concentrations decreased with increased wind speed. High levels of NOₓ were mainly observed when the wind speed was below 2 m s⁻¹. This indicated that local emissions from the busy traffic and heating in the cold season should be the major contributor to observed NOₓ concentrations. The only exception was high NOₓ concentrations observed under easterly winds when wind speed rose in the heating season, suggesting the influence of emission sources in the town center. In Xianghe, wind speed usually experienced a diurnal variation of high wind speed during the day and low values at night. Thereby, local emissions and the diurnal variations
Figure 2  The average diurnal variations of (a) NO/NO\textsubscript{x} ratios; (b) NO\textsubscript{x} concentrations; (c) O\textsubscript{3} concentrations; and (d) SO\textsubscript{2} concentrations in each month from May to November 2013. Monthly averages for each hour and the standard deviations are marked in colors. Black boxes and whiskers represent the 5th, 25th, 50th, 75th, and 95th percentiles.

of advection dilution and the planetary boundary layer were thought to be mainly responsible for shaping the diurnal cycle of NO\textsubscript{x} concentrations and NO/NO\textsubscript{x} ratios. The stronger removal of NO\textsubscript{x} through photochemical reactions during the day may also have played a role in the day/night differences. In the day, active photochemical reactions quickly oxidized freshly emitted NO, leading to a low level of NO/NO\textsubscript{x} ratios, especially in the summer when the temperature and solar radiation favored the photochemical process. After the decreasing of the planetary boundary layer height in the late afternoon, accumulation of NO\textsubscript{x} accelerated and NO\textsubscript{x} concentrations rose dramatically before sunrise on the next day. The sharp increase in night-time NO\textsubscript{x} concentrations found in the cold season was due to significant emissions from heating. The fraction of NO in NO\textsubscript{x} also increased, as a result of less efficient chemical removal and enhanced emissions in the cold season.

3.2  Ozone

The seasonal variation of the secondary gas pollutant, O\textsubscript{3}, was opposite to that of NO\textsubscript{x} (Fig. 2c). The generation of O\textsubscript{3} was effective during the period when the weather was warm and sunlight was plentiful. In contrast, O\textsubscript{3} photochemical production was slowed down in cold weather and O\textsubscript{3} was largely consumed by emitted NO. Thus, the average O\textsubscript{3} concentrations during May and July were almost twice as much as that during September and October. The highest hourly O\textsubscript{3} average was found in May and was close to 240 ppbv, followed by around 160 ppbv in June and July. Compared to the observation in 2005 (Ma et al., 2007), high ozone events were more notable in Xianghe in 2013. The average ozone daily maximum was about 100 ppbv in May, 76 ppbv in June, and 72 ppbv in July. It was found that the days on which the 8-h ozone averages exceeded 80 ppbv accounted for about 55% of the observational days in May and around 30% in June and July, while in September and October, the observed averages did not exceed 80 ppbv. The diurnal cycle of surface O\textsubscript{3} peaked in the afternoon and fell to a low level at night until it reached a minimum in the early morning. At night, the accumulation of primary gas pollutants such as NO aggravated the depletion of O\textsubscript{3}. In particular, the night-time NO\textsubscript{x} concentrations in the fall were extremely high, which led to O\textsubscript{3} being almost completely depleted. After sunrise, the buildup of O\textsubscript{3} concentrations was attributed to the photochemical production and the down-mixing of ozone-rich air.

During the observational period, an O\textsubscript{3} episode was observed during 5 and 7 May, when a stagnant high pressure system stayed on the Huanghai Sea to the east of the site. Under the control of the high pressure ridge, southwesterly and southerly surface winds prevailed over the site (Fig. 4b), bringing the air mass from the city...
cluster in the hinterland of the NCP region and the megacity of Tianjin. As shown in Fig. 4a, the daily maximum \( O_3 \) concentrations on each day of the episode were 165, 193, and 239 ppbv, respectively, which contributed to about 94% of the observed total oxidant (\( O_3 + NO_2 \)) concentrations. The \( O_3 \) levels that exceeded 150 ppbv lasted for 3, 7, and 10 hours on 5, 6, and 7 May, respectively. The high \( O_3 \) concentrations under the influence of southwesterly and southerly winds accompanied by the low level of \( NO/NO_x \) ratios, indicated an aged air mass and suggested that regional transport was the major contributor to the observed high \( O_3 \) level.

Since the total oxidant \( O_x \) is more conservative for analyzing regional transport compared to \( O_3 \), a further investigation of \( O_x \) and winds was performed. A clear dependence of \( O_x \) concentrations on wind speed and wind direction is shown in Fig. 3b. High concentrations of \( O_x \) were mainly observed under west-south wind directions, especially from the south-southwest-southwest sector. The polluted air mass could thereby be brought from the hinterland of the NCP region in the southwest direction, where
a cluster of cities and towns are located. Under south-westerly winds, consecutive \( O_3 \) pollution events could sometimes last for several days. Analysis of the high \( O_3 \) events (defined here as daily maximum hourly average \( O_3 \) concentrations exceeding 120 ppbv and lasting for more than three hours) showed that \( O_3 \) contributed 86%-92% to the observed \( O_3 \) concentrations for ten events during May and July, and 75% for one event in September. The NO/NO\(_x\) ratios during these pollution events were exclusively less than 0.2, suggesting that the air mass was aged and transported from the source areas of the pollutants (Chaloulakou et al., 2008). In contrast, it was relatively quite clean when winds came from the north-east direction. In general, surface \( O_3 \) concentrations rose with increased wind speed, indicating the influence of pollution transport.

### 3.3 Sulfur dioxide

Increased surface \( SO_2 \) concentrations were observed from September to November, probably as a result of enhanced emissions and slowed removal processes. The maximum \( SO_2 \) hourly averages were about 35, 42, and 50 ppbv in September, October, and November, respectively. The average diurnal cycle of \( SO_2 \) concentrations exhibited a pronounced peak of about 10 ppbv around noon (Fig. 2d). A daytime peak of \( SO_2 \) concentrations has previously been observed at a few sites in the NCP (Lin et al., 2012). The diurnal pattern of a single peak appearing at midday instead of double peaks during the morning and evening rush hours could be attributed to the advection transport of an \( SO_2 \)-rich air mass due to a change in wind direction (e.g., Lin et al., 2008, 2009) or the downward mixing from an \( SO_2 \)-rich layer above (e.g., Meng et al., 2008; Chen et al., 2009). The daytime peak of \( SO_2 \) concentrations observed in Xianghe was usually associated with low winds (Fig. 3c). The buildup and drop of the \( SO_2 \) daytime peak generally followed the development of the planetary boundary layer during the day, suggesting that the process of downward mixing might be the major contributor to the daytime peak. During the non-heating period, night-time \( SO_2 \) concentrations were, on average, below 5 ppbv and showed a strong increase in night-time \( SO_2 \) concentrations with increased wind speed under easterly winds (Fig. 3d). During the heating period, high concentrations of \( SO_2 \) could continue from midday to the early morning on the next day, with night-time concentrations close to 10 ppbv. In addition, a second peak, comparable with or even higher than the daytime peak, sometimes occurred around midnight. The \( SO_2 \)-polluted air mass from the southwest and northeast wind sector (Fig. 3e) were thought to be mainly responsible for the observed night-time high concentrations and implied possible emission sources in those directions after the heating began. The influence of transported \( SO_2 \) from emission sources on \( SO_2 \) concentrations in the heating month of November was also supported by a large variability in \( SO_2 \) concentrations throughout the day. Moreover, the daytime peak was found to be less frequent in November than in the other two months, with a few double-peak diurnal patterns.

### 4 Summary

Measurements and analysis of surface \( O_3 \), NO\(_x\), and \( SO_2 \) were carried out from May to November 2013 at a rural site, Xianghe, between the twin megacities of Beijing and Tianjin in the polluted NCP region. During the observational period, NO\(_x\) concentrations ranged from several ppbv to nearly 180 ppbv in the summer and over 400 ppbv in the fall. High NO\(_x\) concentrations mostly occurred under calm conditions, revealing local emissions to be dominant in Xianghe. High ozone episodes were found to be more notable compared with the situation eight years ago, with the highest hourly average close to 240 ppbv in May. The dependence of \( O_3 \) concentrations on winds suggested regional pollution in the NCP. \( O_3 \) concentrations rose with increased wind speed and exhibited high levels mainly in the south-west wind sector, which could bring a polluted air mass from the city cluster in the hinterland of the NCP region in the southwest direction. An average \( SO_2 \) diurnal cycle of a pronounced peak around midday instead of double peaks during the morning and evening rush hours was noted and mainly attributed to the downward mixing from an \( SO_2 \)-rich layer above. A second peak occurred around midnight after the heating began. Emission sources that had an impact on observed night-time high concentrations also differed between the non-heating and the heating months.
Acknowledgements. This work was supported by the National Natural Science Foundation of China (Grant Nos. 41305114 and 41175030). This work was also supported by Beijing Municipal Natural Science Foundation (Grant No. 8121002). We thank Rui Li at the Xianghe site for the careful routine work there.

References


Ge, B. Z., X. B. Xu, W. L. Lin, et al., 2012: Impact of the regional transport of urban Beijing pollutants on downwind areas in summer: ozone production efficiency analysis, Tellus B, 64, doi:10.3402/tellusb.v64i0.17348.


