Evolution of boundary layer ozone in Shijiazhuang, a suburban site on the North China Plain

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ABSTRACT

The structure of the boundary layer affects the evolution of ozone (O₃), and research into this structure will provide important insights for understanding photochemical pollution. In this study, we conducted a one-month observation (from June 15 to July 14, 2016) of the boundary layer meteorological factors as well as O₃ and its precursors in Luancheng County, Shijiazhuang (37°53′N, 114°38′E). Our research showed that photochemical pollution in Shijiazhuang is serious, and the mean hourly maximum and mean 8-hr maximum O₃ concentrations are 97.9 ± 26.1 and 84.4 ± 22.4 ppbV, respectively. Meteorological factors play a significant role in the formation of O₃. High temperatures and southeasterly winds lead to elevated O₃ values, and at moderate relative humidity (40%–50%) and medium boundary layer heights (1200–1500 m), O₃ production sensitivity occurred in the transitional region between volatile organic compounds (VOC) and nitrogen oxides (NOₓ) limitations, and the O₃ concentration was the highest. The vertical profiles of O₃ were also measured by a tethered balloon. The results showed that a large amount of O₃ was stored in the residual layer, and the concentration was positively correlated with the O₃ concentration measured the previous day. During the daytime of the following day, the contribution of O₃ stored in the residual layer to the boundary layer reached 27% ± 7% on average.

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Introduction

Nitrogen oxides (NO\textsubscript{x}) and volatile organic compounds (VOC) emitted from emission sources undergo photochemical reactions in the presence of sunlight, which generates secondary pollutants, such as ozone (O\textsubscript{3}) and peroxy acetonitrile. The reactants involved in photochemical reactions and the resultant mixture are referred to as photochemical smog (Seinfeld and Pandis, 1998). O\textsubscript{3} is an important component of photochemical smog, and it is the main indicator for measuring the intensity of photochemical smog (Seinfeld and Pandis, 1998). O\textsubscript{3} in urban areas not only increases the greenhouse effect (Akimoto, 2003) but also seriously affects the local air quality (Tang et al., 2012, 2017) and causes respiratory diseases in humans and animals (NRC, 1991; Fowler et al., 1997). In addition, O\textsubscript{3} oxidizes chlorophyll cells and decreases plant photosynthesis, thereby affecting the energy balance of the Earth’s atmospheric system (Yue et al., 2017).

The causes of near-ground O\textsubscript{3} accumulation are complicated. Emission sources, meteorological factors (Sillman, 2002; Jenkin and Clemitshaw, 2002), and transport in horizontal and vertical directions (Pisano et al., 1997; Glaser et al., 2003; Velasco et al., 2008) affect the spatial and temporal distribution of O\textsubscript{3}. Meteorological factors, including the temperature (TMP), relative humidity (RH), boundary layer height (BLH), wind speed (WS) and wind direction (WD), play an important role in the formation, sedimentation, transport and dilution of O\textsubscript{3} (Nair et al., 2002; Zhang and Oanh, 2002; Elminir, 2005). For example, elevated O\textsubscript{3} concentrations generally occur on days with strong sunlight and low wind speeds, which favor the photochemical production and the accumulation of O\textsubscript{3} and its precursors (Gao et al., 2005; Ding et al., 2013). Moreover, the WD will also affect the transport of pollutants. For instance, in Beijing, westerly airflows bring clean air masses from the Inner Mongolian region while southerly winds can carry O\textsubscript{3} and its precursors from Hebei and Shandong provinces (Duan et al., 2008; Han et al., 2011). In addition, the BLH is critical for atmospheric diffusion. Previous studies have shown that a low BLH often leads to high O\textsubscript{3} concentrations (NASTRO, 2000), and the nighttime O\textsubscript{3} in the residual layer (RL) will be transported to the ground along with the development of the boundary layer (BL), thus increasing the near-ground O\textsubscript{3} concentration (Neu et al., 1994; Geng et al., 2009; Kaser et al., 2017). Although O\textsubscript{3} formation depends on its precursors (NO\textsubscript{x}, CO, and VOC) and appropriate meteorological conditions, the relationship between O\textsubscript{3} and its precursors is nonlinear. Therefore, strategies need to be formulated according to the characteristics of different regions (Sierra et al., 2013; Kiriyama et al., 2015).

The North China Plain (NCP) is the economic center of China. With rapid economic development, the energy structure has changed, and the number of motor vehicles continues to increase. Contaminants such as CO, VOC and NO\textsubscript{x} emitted from emission sources are transformed into O\textsubscript{3} in the presence of sunlight, which results in increased O\textsubscript{3} concentrations (Crutzen, 1988; Logan, 1985; Houweling et al., 1998; Tang et al., 2009; Ma et al., 2016), especially in areas along the Taihang Mountains. Studies have identified unique meteorological conditions along the piedmont area of the Taihang Mountains (Zhu et al., 2018a); however, few studies have focused on the influence of BL meteorology on O\textsubscript{3}, especially the response of O\textsubscript{3} to the BLH and the contribution of RL transport.

In this study, a one-month long observation was conducted during a period of severe photochemical pollution (June-July) in Shijiazhuang. First, the evolution of O\textsubscript{3} and its precursors in the surface layer will be described. Subsequently, the influence of meteorological factors (TMP, RH, WD and BLH) on O\textsubscript{3} will be explained. Finally, the factors that influence the O\textsubscript{3} concentration in the RL will be clarified and the contribution of RL O\textsubscript{3} to the near-ground O\textsubscript{3} concentration the following day will be evaluated. Our ultimate goal is to provide more accurate control measures for photochemical pollution in the NCP.

1. Methods and data

1.1. Measurement site

The site for this study was located in the courtyard of the Luancheng Meteorological Bureau (37°53′N, 114°38′E), which is in the southeast of Shijiazhuang, adjacent to Shiluan Street, National Highway 308. The surroundings are residential areas and the important emission sources are motor vehicles. The ground conditions of the site are typical of urban underlying surfaces, which basically reflect the air pollution situation in Shijiazhuang. Our study was conducted in summer from June 15 to July 14, 2016.

1.2. Experimental instruments

1.2.1. Near-ground observation instruments

The O\textsubscript{3}, NO\textsubscript{x} and CO instruments used in this experiment were manufactured by the Thermo Fisher Scientific Company of USA (Tang et al., 2009, 2012), and the instrument properties are presented in Appendix A Table S1. Briefly, O\textsubscript{3} was measured with a 49C ultraviolet spectrophotometry O\textsubscript{3} analyzer (49i, Thermo Fisher Scientific, USA), which is based on the principle that O\textsubscript{3} can absorb ultraviolet ray at a wavelength of 254 nm. The extent to which ultraviolet light is absorbed in this wavelength is directly related to the O\textsubscript{3} concentration. Therefore, we can rely on the degree of absorption to calculate the O\textsubscript{3} concentration. NO\textsubscript{x} was measured with a 42CTL high-precision chemiluminescence NO-NO\textsubscript{2}-NO\textsubscript{3} analyzer (42i, Thermo Fisher Scientific, USA), which is based on the principle that NO\textsubscript{x} can absorb ultraviolet light at a wavelength of 254 nm. The extent to which ultraviolet light is absorbed in this wavelength is directly related to the NO\textsubscript{x} concentration. Therefore, we can rely on the degree of absorption to calculate the NO\textsubscript{x} concentration. When NO\textsubscript{2} is detected, NO\textsubscript{2} is converted to NO by a molybdenum converter and then quantitatively analyzed by a chemiluminescence reaction. CO was measured with a 48i gas-filter correlation infrared absorption CO analyzer (48i, Thermo Fisher scientific, USA). The measurement principle is based on the fact that CO...
absorbs infrared light at a wavelength of 4.6 μm, and the CO concentration is calculated by detecting how much infrared light is absorbed when the sample gas passes through the detector.

In this study, near-ground meteorological data were obtained from the Luancheng Meteorological Bureau, and they include the TMP, RH, WD and WS. All the meteorological data were qualified by the China Meteorological Administration.

1.2.2. Boundary layer observations
The BLH in this experiment was measured by an enhanced single-lens ceilometer (CLS51, Vaisala, Finland) (Tang et al., 2015), which is based on strobe laser lidar (laser detection and range measurement) technology. The detection wavelength was 910 nm, the detection range was 7.7 km and the temporal and vertical resolutions were 16 sec and 10 m, respectively. The BLH was determined by the gradient method based on the backscatter density. We calculated the BLH by determining the location of the maximum (−dβ/dz) based on the vertical gradient of the attenuated backscattering coefficient (Tang et al., 2016; Zhu et al., 2018b). A previous study (Tang et al., 2016) reported that the BLH is overestimated during sand-dust crossing. In addition, when it rains, the BLH data observed by the ceilometer are not accurate. In this study, we eliminated the data collected during dust, strong wind and precipitation periods.

1.2.3. Tethered balloon detection system
The vertical profiles of meteorological factors and O3 were measured by an XLS-II tethered balloon detection system (XLS-II, Institute of Atmospheric Physics, Chinese Academy of Sciences, China), which was developed by the Institute of Atmospheric Physics, Chinese Academy of Sciences (Bian et al., 2007; Sun et al., 2017). This system consists of a tethered balloon, sensor and data processing components (collection, transmission and reception). In this study, a miniaturized ozonesonde (Institute of Atmospheric Physics, Chinese Academy of Sciences, China) was carried on a tethered balloon to obtain the vertical distribution of the O3 concentration, TMP, RH, WD, WS and other meteorological parameters. The detection signal was transmitted to the computer in real time via wireless mode. We carried out the experiment twice a day, with one measurement series in the morning before the development of the BL and the other at noon time, which coincided with the highest concentration of O3. Sunrise occurs at approximately 5:00 local time (LT) during June and July in Shijiazhuang, although the BL starts to develop at approximately 8:00 LT (Appendix A Fig. S1). Therefore, the experiment in the morning usually ended before 8:00 LT and the detailed times of the flights are shown in Table 1. During the experiment, one flight lasted approximately 1 hr. The average ascending or descending speed was approximately 0.6 m/sec. The maximum height of the flights was approximately 1200 m.

The principle underlying the miniaturized ozonesonde is that when the outside air passes through a potassium iodide solution, O3 in the air reacts with KI to generate iodine gas:

\[2KI + O_3 + H_2O \rightarrow 2KOH + I_2 + O_2\]  

If two electrodes are inserted into the solution and a small voltage (12 V) is added to the cathode, the I2 molecule will move toward the cathode and become ionized in its vicinity:

\[I_2 + 2e^- = 2I^-\]  

Then, these iodine ions migrate to the anode and are oxidized to iodine molecules under the action of an electric field:

\[2I^- - 2e^- = I_2\]  

The ion current (migrating charge) is quantified according to the amount of ozone that reacts with the solution per unit time. Therefore, the O3 concentration in the atmosphere can be obtained by measuring the current flowing in the solution.

1.2.4. Cross-validation for BLH and ozone
Based on the sounding data in the morning and at noon, the BLH was also retrieved by the vertical profiles of the virtual potential temperature (VPT), WD and WS using the method of Tang et al. (2016) (Appendix A Fig. S2). Subsequently, the BLH data retrieved by the ceilometer were compared with the data from the radiosondes. The correlation coefficient was higher than 0.9, which indicated that the BLH observed by the ceilometer was reliable and could be applied to this experiment (Appendix A Fig. S3).

Bian et al. (2007) indicated that the observations of the XLS-II tethered balloon detection system are highly consistent with Vaisala’s ozonesonde in the troposphere. We only studied the ozone variation in the BL; therefore, the results were credible. To ensure the consistency of these measurements with that of the near-surface observation instrument, we also compared the thermoelectric instrument O3 data with those of the ozonesonde below 5 m. In this experiment, the time resolution of the thermoelectric instrument and the ozonesonde was 5 min and 1 sec, respectively. Therefore, the ozonesonde data were processed based on a 5-min average, and the two sets of data were linearly fitted. The results showed that the correlation coefficient between the two sets of data was 0.9 (Appendix A Fig. S4). Therefore, the ozonesonde O3 data are in good agreement with those measured using the thermoelectric instrument. Based on the fitted

<table>
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<th>RL column (mg/m²)</th>
<th>Total column (mg/m²)</th>
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<td>Average contribution</td>
<td>27% ± 7%</td>
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equation, we corrected the ozonesonde O3 observations and acquired eight profiles of O3.

2. Results and discussion

2.1. Concentrations of air pollutants

First, the time series of ground-level meteorological factors (TMP, RH, BLH, WD and WS), O3 and its precursors were analyzed as shown in Fig. 1. The O3 concentration had a clear diurnal variation and presented low and stable values in the morning and increasing values as the solar radiation and temperature increased, with its peak occurring from 13:00 to 15:00 LT. These variations were consistent with the generally observed results documented in previous studies (Zhang and Trivikrama Rao, 1998; Ma et al., 2013). During the observation period, the mean hourly maximum and mean 8-hr maximum O3 concentrations were 97.9 ± 26.1 and 84.4 ± 22.4 ppbV, respectively. According to the “Ambient Air Quality Standard” (GB3095-2012), the number of days for which the O3 concentrations exceeded the national 1- and 8-hr maximum standards was 17 and 19 days, respectively, which accounted for 57% and 63% of the total number of days, respectively. The mean 8-hr maximum O3 concentration was 123.3 ppbV, which is 1.6 times higher than the national standard, indicating severe photochemical pollution in Shijiazhuang in summer.

The precursors of O3 were also analyzed in the experiment. Because of the lack of VOC measurements, we used CO instead because it is strongly correlated with VOC (Stephens et al., 2008). As shown in Fig. 1, the diurnal changes in CO showed a bimodal pattern, with the first peak observed from 7:00 to 9:00 LT followed by a gradual decrease to a trough at 15:00 LT and the second peak observed from 18:00 to 22:00 LT. This result is consistent with previous studies (Tang et al., 2009, 2012), and the observed pattern was mainly driven by automobile emissions. During the observation period, the changes in NO, NO2, NOx and CO were pronounced, and ranged from 0.1 to 147.3, 0.0 to 81.3, 5.8 to 191.0 and 148.0 to 3022.0 ppbV, respectively. The corresponding daily average concentrations were 9.2 ± 8.5, 23.1 ± 5.4, 32.4 ± 12.5 and 900.0 ± 270.0 ppbV, which indicated high concentrations of O3 precursors.

2.2. Impacts of boundary layer meteorology

To explain the causes of severe photochemical pollution, we analyzed the meteorological factors related to the O3 concentration. To avoid interference from diurnal variations in O3 and meteorological factors, we analyzed the relationship between meteorological factors and air pollutants using the daytime averages (from 10:00 to 17:00 LT).

Studies have shown that TMP is positively correlated with O3 (Satsangi et al., 2004), which is consistent with the results shown in Fig. 2a. Following the increase in TMP, O3 also showed an upward trend because the increase in TMP usually enhances the production of O3 in the atmosphere. In general, WS will affect the diffusion of air pollutants; however, it was slow, at less than 3.0 m/sec during the observation period (Fig. 1), and will not be further discussed in this study. However, we studied the impact of the WD on the O3 concentration. As shown in Fig. 2b, at low O3 concentrations (<70 ppbV), a southwesterly wind prevailed near the ground. When the O3 concentration exceeded 80 ppbV, the prevailing wind was a southeasterly wind. Shijiazhuang is located on the leeward side of the Taihang Mountains. When the southeasterly wind prevails, it is blocked by the mountains, thus leading to the continuous accumulation of pollution; however, when the westerlies prevail, outward transport and diffusion of pollutants are observed. High radiation (RAD), low RH and low BLH have been shown to be important dynamic features in the production of O3 (NARSTO, 2000), although these
phenomena were not observed in this study (Appendix A Fig. S5). To clarify the effects of the RAD, RH and BLH on O₃ concentrations, the following sections provide a more in-depth discussion.

2.3. Evolution of ozone sensitivity with boundary layer meteorology

The BLH refers to the near-ground height that can be reached in the process of mixing due to thermal buoyancy or mechanical force and it is one of the main factors that affect atmospheric diffusion, which is related to the RAD (Tang et al., 2016). As the RAD increased, the turbulence in the BL increased, resulting in a high BLH. Therefore, although strong RAD is beneficial to O₃ formation, high BLH is always accompanied by strong RAD, which enhances the atmospheric diffusivity and results in low O₃ concentrations in the BL (Fig. 3a). RH reflects the ratio of vapor pressure to saturated vapor pressure in the atmosphere and plays an important role in the photochemical reaction (O(1D) + H₂O → 2OH). The relationships among the BLH, RH and O₃ concentrations are shown in Fig. 3b. With an increase in the BLH, the RH showed a downward trend while the O₃ concentration showed an initially increasing and then decreasing trend. At a moderate BLH (1200–1500 m) and moderate RH (40%–50%), the O₃ concentration reached a maximum value. Therefore, the meteorological conditions at this time were the most conducive to O₃ formation. However, this result is inconsistent with that of previous studies in which high O₃ concentrations corresponded to a low BLH, because of the particular photochemical pollution in the NCP (NARSTO, 2000).

To identify the mechanisms underlying the response of O₃ to BLH and RH, we hypothesized that changes in meteorological factors can lead to precursor changes, which affect O₃ production. To verify the above statements, we analyzed the O₃ production sensitivity at different BLHs (Fig. 4). When the BLH was less than 1200 m, the CO/NOₓ ratio was high. Therefore, O₃ production was sensitive to NOₓ, which corresponded to the NOₓ limitation. When the BLH was between 1200 and 1500 m, the CO/NOₓ ratio was moderate, the air parcel was in the transitional region between the VOC and NOₓ limitations, and the O₃ concentration reached its peak. When the BLH exceeded 1500 m, although the CO and NOₓ concentrations gradually decreased, the degree of CO reduction was much greater than that of NOₓ (Appendix A Fig. S6), resulting in a gradual decrease in CO/NOₓ which corresponded to the VOC limitation. A schematic diagram of
the relationship between meteorological factors and O3 production sensitivity is summarized in Fig. 5. Once the forecast reveals that a moderate RH and BLH and high TMP will occur, photochemical pollution warnings need to be initiated. However, considering the lack of VOC observations, this conclusion still needs to be confirmed via synchronous observations of VOC, NOx and O3 in the future.

2.4. Vertical evolution of O3

2.4.1. O3 profile analysis

The above analysis shows that the daytime O3 concentration was closely related to the evolution of the BLH. At night, the BLH is usually low, and a large amount of NO emissions leads to lower O3 concentrations in the stable boundary layer (Hidy, 2000; Solomon et al., 2000; Lin et al., 2007). However, due to the blocking of the stable boundary layer, the O3 in the RL is preserved. We used vertical O3 profiles to explain the following two phenomena: the cause of O3 concentration evolution in the RL; and the impact of O3 stored in the RL on the development of O3 in the BL.

To achieve these aims, the O3 profiles were observed on the most polluted days, including 20, 21, 22 and 29 June (Fig. 6). In the morning, an apparent stratification of O3 profiles occurred. The O3 concentration in the BL was generally low, with an average concentration of 20 ppbV. NO titration occurred, resulting in a reduction of near-ground O3. However, the O3 concentration in the RL rose sharply as the height increased, and the maximum value reached 100 ppbV (except on 29 June) because a large amount of the O3 generated in the photochemical reaction occurred in the BL on the previous day and remained in the RL at night. To verify this supposition, we performed a correlation analysis between the O3 concentration in the RL and the maximum O3 concentration on the previous day and found a positive correlation (correlation coefficient of 0.7; Fig. 7). This finding indicated that higher O3 concentrations in the BL on the previous day corresponded to higher O3 concentrations in the RL on the following day.

The noon profiles show that the O3 in the BL was evenly distributed and presented a high concentration that ranged from 120 to 140 ppbV. Two reasons explain this phenomenon: the near-ground NOx and other precursors continued to accumulate before sunrise, which provided abundant precursors for the photochemical reaction to produce O3, and solar radiation enhanced NO2 photolysis after sunrise to generate...
then reacted with O₂ in the air to generate O₃; and O₃ in the RL (O₃ (max)) on the previous day and the O₃ concentration in RL.

Dry deposition is (and the contribution of the photochemical reaction plus
noon BL is 95%, the remaining O₃ concentration of 68% was from chemical processes and dry deposition. However, if the RL transport at noontime was not considered, then the contribution of the photochemical reaction plus dry deposition should be 95%. Therefore, using only near-ground observations will overestimate the photochemical production of O₃ and vertical gradient observations play a crucial role in the formulation of O₃ control programs. Moreover, since the O₃ concentration on the previous day will affect the midday high value of the following day, the forecast and early warning of O₃ must be carried out in advance to ensure that severe pollution processes meet the national standards.

Nevertheless, one disadvantage of this study is that we only considered the contribution of O₃ in the RL and ignored the influence of the storage of precursors and subsequent photochemical conversion. Therefore, our next step will be to simultaneously detect O₃ and its precursor concentrations to accurately quantify the effect of contaminants in the RL on atmospheric photochemical pollution.

3. Conclusions

In this study, a one-month enhanced observation was carried out in Shijiazhuang in 2016. This study focused on analyzing the effect of meteorological factors and RL transportation on the near-ground O₃ concentrations. The following main conclusions were drawn.

Photochemical pollution in Shijiazhuang is serious in summer, and the O₃ concentration exceeded the standard by approximately 60% in this study. A good correlation was observed between TMP and O₃ concentrations. In addition, southeasterly winds increased the accumulation of O₃ in the piedmont region of the Taihang Mountains. Moreover, we found that a low BLH did not lead to elevated O₃ values, as indicated in previous studies, and moderate RH (40%–50%) and a medium BLH (1200–1500 m) corresponded to high O₃ days, which was primarily because O₃ production sensitivity differed under different meteorological conditions. O₃ production sensitivity shifted from the NOₓ limit to the VOC limit as the BLH increased, and the O₃ control strategy should be changed from NOₓ to VOC emissions.

Combined with the vertical profiles of O₃, we found that a large amount of O₃ was stored in the RL, and the concentration was positively correlated with the O₃ concentration on the previous day. With the development of the BLH, O₃ in the RL was transported to the BL, and its contribution reached 27% ± 7% on average. These results are very important for discerning the influence of the boundary layer structure on the O₃ concentrations over the NCP.

Acknowledgments

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Appendix A. Supplementary data

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REFERENCES


