Dual-height Distribution of Ozone and Nitrogen Oxides during Summer in Urban Tianjin: An Observational Study

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ABSTRACT

Measurements of gaseous pollutants, including ozone (O_3) and nitrogen oxides (NO_x), were simultaneously conducted at 220 m (via the installation of an air flow drainage system on a 255-m meteorological tower) and 3 m above the ground in urban Tianjin during summer 2018. The observed O_3 concentrations at the two altitudes exhibited similar diurnal variations but distinctly different values, with higher levels near the surface during the day and the opposite trend at night. Generally higher concentrations of NO and NO_2 were found at 3 m than 220 m, and the difference in concentration between the two altitudes for the latter pollutant was smaller during daytime and highest at night. O_x ($O_3 + NO_2$) concentration near the surface during the day, but the difference was negligible at night. Based on the higher NO_x level at 3 m, the photochemical production of O_3 (O_x) at low altitudes intensified during the day, suggesting that the O_3 surface concentration was mainly influenced by local photochemical production. Additionally, by measuring the reactive nitrogen (NO_y) near the surface and calculating NO_z ($NO_y - NO_x$), the ozone production efficiency (OPE; O_x/NO_z) in urban Tianjin was assessed for the first time and determined to be 6.0 ± 0.4 . Compared to the values measured during summer 2010, lower levels of NO_x but significantly higher ones for O_3 were observed during the same season in 2018.

Keywords: Nitrogen oxides; Ozone; Vertical observation; Ozone production efficiency.

INTRODUCTION

Tropospheric ozone (O_3) exerts a large impact on air quality, environment, and climate change (Tang *et al.*, 2006). Along with rapid economic growth and urbanization, emissions of gaseous pollutants including O_3 precursors have largely increased in China. As a result, O_3 pollution has become increasingly serious at the urban and regional scales. In the densely populated and economically developed regions of China, such as the Yangtze River Delta, Pearl River Delta, and Beijing-Tianjin-Hebei region, O_3 has become a major air pollutant during summer and autumn (Lam *et al.*, 2005; Wang *et al.*, 2006; Ding *et al.*, 2008; Ran *et al.*, 2009; Lu *et al.*, 2010; Tang *et al.*, 2011).

Tropospheric O_3 is mainly formed by photochemical reactions of its precursors, nitrogen oxides (NO_x), and volatile

organic compounds (VOCs) in the presence of sunlight (Haagen-Smit, 1952; Sillman, 2002; Zou *et al.*, 2015). Variations in surface O_3 and NO_x concentrations are not only influenced by precursor emissions and photochemical processes but also by transport processes and boundary layer evolution. The advective transport of air pollutants is influenced by the dominant wind direction and topography. Vertical exchange of air pollutants includes both downward transport from high altitude and upward turbulent mixing from the ground. Information on the vertical exchange of air pollutants only based on measurements near the surface can be difficult to obtain. Therefore, obtaining vertical measurements is necessary to understand the characteristics of O_3 more thoroughly and its precursors within the boundary layer.

Given the limitations of the current techniques, continuous online monitoring of the vertical distribution of air pollutants within the urban boundary layer is usually based on meteorological towers. Some studies on the vertical profiles of air pollutants such as O_3 , NO_x , carbon monoxide (CO), sulfur dioxide (SO_2), particulate matter (PM) and peroxyacetyl nitrate (PAN) in the North China Plain have been based on either the 325-m meteorological tower in Beijing (Liu and

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Hong, 2000; Meng *et al.*, 2002; An *et al.*, 2003; Ding *et al.*, 2005; Sun *et al.*, 2006; An *et al.*, 2007; Ma *et al.*, 2007; Sun *et al.*, 2010) or the 255-m meteorological tower in Tianjin (Han *et al.*, 2009; Huang *et al.*, 2009; Sun *et al.*, 2010; Qiu *et al.*, 2019; Yao *et al.*, 2019). A difference in the concentrations of air pollutants at different heights was noted within the boundary layer. However, due to the limited space and uncontrollable conditions on the tower, the online instruments placed at different heights of the towers are usually not sufficiently maintained to ensure adequate data quality. Additionally, data quality is also restricted by the fluctuation of instrument response with time and the parallelism between instruments. Passive sampling devices are relatively simple, but present low time resolution as a drawback.

Tianjin is located in the North China Plain, where tropospheric O₃ is found to be at a considerably high level (Xu and Lin, 2010). O₃ pollution has become more severe during the past decades (Li *et al.*, 2019; Lu *et al.*, 2019). Urbanization, economic development, and rapid increase in the number of vehicles (more than 2.88 million in 2018 in Tianjin) caused significant anthropogenic ozone precursor emissions. Therefore, conducting long-term observations of O₃ and its precursors at different heights in Tianjin area is crucial. Such studies can provide a scientific basis for taking reasonable and effective measures to mitigate O₃ pollution. In this study, an air flow drainage system at a high altitude was built on the 255-m meteorological tower in urban Tianjin. Online instruments on the ground were able to sample air from high altitudes almost without any loss. Concentrations of O₃ and NO_x were simultaneously measured at a height of 220 m and 3 m above ground level to study the characteristics of these gases at different heights.

METHODS

The observational site is located in the yard of Tianjin

Atmospheric Boundary Observatory (TABO) of the China Meteorological Administration (39°06'N, 117°10'E, 2.2 m a.s.l.), which is in the southern part of urban Tianjin. It is surrounded by residential and commercial areas and is approximately 100 m away from a freeway to its north.

An air drainage system (Fig. 1) with the inlet placed at a height of 220 m above ground level was situated on the 255-m-high meteorological tower in TABO. Air from a height of 220 m could be drained into a Teflon tube and eventually entered the online instruments in an air-conditioned room on the ground. The air drainage system mainly contains a large-caliber Teflon tube (Shanghai Huzhuang Rubber Plastic Products Co., Ltd., China) with an I.D. of 3.2 cm and an O.D. of 3.6 cm and a rotary vane pump (GAST1423-101Q-G626X; Gast Manufacturing, Inc., USA) with a free air flow of 20 m³ h⁻¹ under an air pressure of approximately 1 bar. To prevent the entry of rain and insects into the pipeline, a protection cover was equipped in front of the inlet. The Teflon pipe was wrapped using aluminum foils to shield it from sunlight. The retention time of the air in the drainage system was less than 35 s. An air flow distributor with eight branch pipes was installed between the pipe and the pump. Through the branched pipes, air could be sampled and analyzed using different instruments. A pressure meter probe was also placed in the distributor to monitor the air flow pressure. Difference in pressures between the inlet (at 220 m high) and the distributor was less than 20 hPa. Condensed water (if any) in the buffer bottle could be automatically drained off by a little pump (Shenzhen Sypda Technology Co., Ltd., China) to prevent water from accumulating in the pipe and entering the analyzers. The rotary vane pump was protected by a high-volume particulate filter. Using a time controller and 3-way solenoid valve, air at 220 m, surface air, zero gas, and span gases could be subsequently switched in the analyzers. Accordingly, gas pollutants at different heights could be conveniently measured near the surface.

Fig. 1. An air flow drainage system based on a 255-m-high meteorological tower in urban Tianjin.

Instrument calibration and maintenance could also be easily performed on the ground. This system helps in overcoming the space limit of the tower.

Field observations of O₃, NO₂, and NO at two heights were obtained using this air flow drainage system from June 1 to August 31, 2018. The air-sample collection was switched every 15 min between 220 m and 3 m. Reactive nitrogen (NO_y) was only measured near the surface because NO_y compounds other than NO must first be transformed into NO before they can be measured using chemiluminescence. They were converted to NO by using a molybdenum converter heated to approximately 375°C. NO_y includes all reactive oxides of nitrogen (i.e., NO, NO₂, NO₃, N₂O₅, HNO₂, HNO₃, PAN, organic nitrates, and aerosol nitrates). To minimize the loss of NO_y prior to measurement, an external molybdenum converter was used to limit sample transport time and surface contact area. Thus, the external converter was only deployed near ground level. Data were recorded every 1 min. Information on the gas analyzers is presented in Table 1.

Three aspects of quality control were considered during the measurement:

- (1) To determine the effect of gas loss in the pipeline, O₃ loss test was performed. From August 16 to September 30, 2017, O₃ concentrations at the inlet and outlet of the pipeline were tested in parallel by using two O₃ analyzers. Comparison between measurement results (Fig. 2) from two instruments revealed the negligible loss of O₃ in the

pipeline.

- (2) Standard gases were used to calibrate the instruments. The O₃ analyzer was calibrated using an O₃ calibrator (Model 49i-PS; Thermo Fisher Scientific, USA). An NO/N₂ mixed reference gas (Beijing Huayuan Gas Chemical Co., Ltd., China), gas dynamic calibrator (Model 146i; Thermo Fisher Scientific, USA), and zero-gas generator (Model 111i; Thermo Fisher Scientific, USA) were used for multipoint calibration of the NO_y instrument and for the NO₂ analyzer through the gas-phase titration method.
- (3) Data correction and rejection were performed. Original data was corrected using multipoint calibration results. Each time the sampled air was switched from one height to another, a balancing time of 2 min was required, and the corresponding data was eliminated. The corrected data were further processed into hourly averages for subsequent analysis.

RESULTS AND DISCUSSION

Variations in O₃, NO, and NO₂ at Different Heights

Fig. 3 displays the time series of O₃ concentrations at different heights during the observational period. The missing data are due to instrument calibration, instrument malfunction, power failure, station renewal program, etc. Apparently, the variations in O₃ concentrations at two heights basically shared a similar diurnal pattern, with high values in the daytime

Table 1. Information on instruments.

Gas	Instrument	Manufacturer	Minimum detection limit	Principle of the instrument
O ₃	Model 49i	Thermo Fisher Scientific, USA	0.5 ppb	UV photometry
NO ₂	LGR's NO ₂ Analyzer	Los Gatos Research, Inc., USA	0.01 ppb	Cavity-enhanced laser absorption spectroscopy
NO/NO _y	Model 42i-Y	Thermo Fisher Scientific, USA	0.05 ppb	Chemiluminescence with Mo-converter

Fig. 2. Relationship between O₃ concentrations at the inlet and outlet of the airflow drainage system.

Fig. 3. Time series of O₃ concentrations at different heights in urban Tianjin.

and low values at night. Influenced by weather processes, O₃ concentrations experienced several accumulation-decline cycles, each usually lasting for 7–10 days. Overall, there were 131 hours of O₃ concentrations exceeding 100 ppb from the 1673-h valid data near the surface and 121 hours of O₃ concentrations exceeding 100 ppb from the 1864-h valid data at 220 m.

Table 2 presents the descriptive statistics of O₃, NO₂, NO, and O_x concentrations at two sample heights. A one-to-one correspondence between the data for the two heights was adopted to improve the reliability of the comparison.

The statistical analysis of O₃ concentrations at different heights is also presented in Fig. S1. Surface O₃ level was greater than that at high altitude toward the higher end of the concentration distribution (e.g., the 95% highest value was 109.2 ppb near the surface and 104.1 ppb at 220 m). By contrast, surface O₃ level was lower than that at high altitude toward the lower end of the concentration distribution (e.g., the 5% lowest value was 10.3 ppb near the surface and 15.8 ppb at 220 m). The average (53.2 ± 30.6 ppb) and median (48.8 ppb) values of surface O₃ concentrations were slightly lower than the average (53.8 ± 27.7 ppb) and median (49.9 ppb) values at 220 m. The difference between the daily mean O₃ concentrations at 3 m and 220 m ranged from -18.0 ppb to 12.0 ppb. Variations in daytime O₃ concentration were mainly influenced by processes such as transport (advection or vertical mixing), photochemical reaction, and deposition. High O₃ concentrations were mainly noted during the afternoon, and low O₃ concentrations were mainly noted during the night. Surface concentration was lower than that at 220 m during the night, indicating that near-surface O₃ may be consumed through NO titration more easily than that at 220 m (Han *et al.*, 2009). This result differs from that reported by Sun *et al.* (2010), who measured O₃ concentration at three heights (40 m, 120 m, and 220 m) in the same tower from August 18 to September 22, 2006; they found that O₃ concentration always increased with height. The difference in the vertical distributions between 2006 and 2018 may have been due to the substantial changes in

population, urbanization, and pollutant emission in Tianjin.

Figs. 4 and 5 display the time series of hourly mean NO₂ and NO concentrations at different heights during the observational period. Obvious diurnal variations were observed, with a higher level during the night than in the daytime. NO peaked almost at the same time at different heights, whereas NO₂ peaked at different times, with a later appearance of the maximum concentration at 220 m. According to the statistical results shown in Table 2 and Fig. S2, NO₂ concentration near the surface was significantly higher than that at 220 m for all conditions. NO concentration near the surface was obviously higher than that at 220 m toward the higher end of the concentration distribution, but remained comparable to that at 220 m toward the lower end of the concentration distribution.

The average value of the surface NO₂ hourly mean (± 1 standard deviation) was 15.36 ± 8.15 ppb, with a median value of 14.17 ppb. The mean value of NO₂ at 220 m was 10.98 ± 6.34 ppb, with a median value of 9.40 ppb. The average value of the surface NO was 1.65 ± 3.22 ppb, with a median value of 0.92 ppb. The average value of the high-altitude NO was 1.13 ± 1.40 ppb, with a median value of 0.86 ppb. A two-sided reduced major axis regression was conducted for NO₂ and NO at different heights. The slopes of NO₂/NO were 2.35 ± 0.07 ($R^2 = 0.156$, $P < 0.05$) near ground level and 4.45 ± 0.12 ($R^2 = 0.244$, $P < 0.05$) at 220 m. Higher NO₂/NO values indicated more photochemically aged air mass at 220 m. The average value of surface NO was significantly higher than the median value and considerable amounts of newly emitted NO were observed near ground level, suggesting the effects of local pollution.

Diurnal Variations

Fig. 6 depicts the average diurnal variations of O₃, NO₂, O_x (O₃ + NO₂), and NO at 3 m and 220 m during the observational period. In general, similar diurnal variations were found at different heights for each of the gases.

O₃ increased rapidly after sunrise and maintained a high value between 12:00 and 16:00. Thereafter, the concentration

Table 2. Descriptive statistics of O_x, O₃, NO₂, and NO concentrations at two heights.

	O _x		O ₃		NO ₂		NO	
	3 m	220 m	3 m	220 m	3 m	220 m	3 m	220 m
Mean (ppb)	69.4	65.8	53.2	53.8	15.36	10.98	1.65	1.13
SD (ppb)	27.0	26.2	30.6	27.7	8.15	6.34	3.22	1.40
Min (ppb)	14.9	11.4	3.7	3.7	2.58	0.54	0.11	0.11
P5 (ppb)	33.6	30.6	10.3	15.8	4.86	3.81	0.39	0.39
P25 (ppb)	48.0	45.2	28.9	31.3	9.31	6.38	0.64	0.60
Median (ppb)	65.1	62.8	48.8	49.9	14.17	9.40	0.92	0.86
P75 (ppb)	87.4	83.0	74.1	72.9	20.11	14.13	1.46	1.13
P95 (ppb)	119.2	112.5	109.2	104.1	30.28	23.08	4.55	2.58
Max (ppb)	185.1	181.3	176.9	174.7	52.68	42.08	45.18	23.61
Count (hour)	1550	1550	1673	1673	1550	1550	987	987

Fig. 4. Time series of NO₂ concentrations at different heights in urban Tianjin. **Fig. 5.** Time series of NO concentrations at different heights in urban Tianjin.

began to decline until the early hours of midnight. During the day (08:00–17:00), O₃ concentration was higher near ground level than at 220 m (the average difference was 4.0 ppb, and the maximum difference was approximately 6.0 ppb; Fig. 6(a)). The daytime variations of vertical O₃ distribution differed from those reported in previous studies.

Sun *et al.* (2010) reported that O₃ concentration increased with height, with a considerably higher O₃ gradient during the night than during the daytime. These measurements were taken from August 18 to September 22, 2006. Han *et al.* (2009) and Huang *et al.* (2009) reported similar variations with measurements taken during September–November

2006 and August 4–24, 2007, respectively. Qiu *et al.* (2019) reported very similar O_3 values at two heights during 09:00–16:00 and higher values at higher altitudes after 16:00 during September 2018. These results were observed at the same site but during different years and seasons, which may have resulted in complex changes in the vertical variation in O_3 concentration during different periods in urban Tianjin. Further exploration involving measurements of VOCs is warranted. At night (21:00–06:00), surface O_3 concentration was lower than that in the upper level (an average difference was 7.0 ppb and the highest was close to 9.0 ppb), although the difference seems less than that in 2006 (30–50 ppb; Han *et al.*, 2009; Sun *et al.*, 2010). During early morning (around 07:00) and in the evening (17:00–20:00), O_3 concentrations at different heights were nearly the same. As seen in Fig. 6, O_3 concentrations at different heights began to rise in the early morning. Sunrise during summer was at about 05:00, when the boundary layer begins to elevate. Air in the upper layer (or residual layer) started to mix downward with the air in the lower layer, resulting in a rise in the O_3 concentration near the surface and more uniform distribution through different layers. Along with the further development of the boundary layer under stronger and stronger solar radiation, surface O_3 gradually exceeded aloft O_3 through the photochemical generation. Evidently, the photochemical production of O_3 near the surface was higher than that at higher altitudes, especially during 08:00–17:00 when photochemical reactions were active. Near ground level, O_3 may be more easily depleted through deposition than at 220 m. If the O_3 concentration is higher in the upper level, then the surface O_3 cannot be increased through downward mixing. More O_3 precursors near ground level might be essential for determining the difference in vertical O_3

concentration during the daytime.

The diurnal variation in NO_2 concentration (Fig. 6(b)) shows morning and evening peaks around 07:00 and 19:00, respectively. This was particularly evident at 220 m. Surface NO_2 concentration remained relatively high after 19:00. NO_2 concentration gradually decreased before noon and reached the lowest during 12:00–16:00, contrary to the variation in the O_3 concentration. In general, NO_2 concentration near the surface was higher than that at 220 m, but the two were comparable during the day. The difference between NO_2 concentrations at different heights increased during the night, with the maximum exceeding 9 ppb, possibly due to the accumulation of emitted NO_2 near the ground and weak vertical mixing.

From Fig. 6(d), the diurnal variation of NO is noted to be characterized by a unimodal type, with a peak during 06:00–10:00 and a higher level at night than in the day. The time when NO concentration peaked during early morning was slightly different for different heights. The concentration of NO near the surface was higher than that at 220 m, with the largest difference during the day and the smallest at night. Therefore, O_3 was significantly affected by chemical titration of NO at night, especially near the surface, leading to a much higher level at 220 m than near the surface. In 2006, the average diurnal change of NO_x is with an evident peak around 14:00 (Sun *et al.*, 2010), but this afternoon peak is not found in 2018.

In cities, O_x ($O_x = O_3 + NO_2$) is usually used to represent the total oxidant in the atmosphere. Being more conservative than O_3 , O_x can better characterize the photochemical process, as rapid NO_x - O_3 cycle (Liu, 1977; Nunnermacker *et al.*, 1998) need not be considered. As seen in Fig. 6(c), O_x showed similar variation as O_3 , except the small difference in O_x at

Fig. 6. Average diurnal variations of O_3 , NO_2 , O_x ($O_3 + NO_2$), and NO concentrations at different heights during the observational period.

different heights during the night (especially from midnight to early morning). The concentration increased rapidly after sunrise and reached the maximum at approximately 16:00. The peak of the mean concentration was 87.6 ppb at 220 m and 92.6 ppb near the surface. During the day, the O_x concentration was considerably higher near ground level than at 220 m, with the maximum difference exceeding 6 ppb. As shown in Table 2, for the 1550 pairs of hourly mean O_x concentrations, the average (69.4 ± 27.0 ppb), median (65.1 ppb), minimum (14.9 ppb), and maximum (185.1 ppb) values of surface O_x concentration were 3–4 ppb higher than the average (65.9 ± 27.0 ppb), median (62.8 ppb), minimum (11.4 ppb), and maximum (181.3 ppb) values at 220 m. Therefore, total oxidant production was considerably stronger near ground level than at 220 m during summer in urban Tianjin.

According to the aforementioned analysis, the concentration of O_3 precursor, NO_x , was higher near the surface than at 220 m in urban Tianjin. During the day, photochemical generation of O_3 (O_x) was greater than that at 220 m. Thereafter, the rapid increase in the O_3 concentration was mainly affected by local photochemical formation and not by downward mixing of the residual layer. From 07:00 to 14:00, O_3 concentration on an average increased to approximately 50 ppb near the surface and 46 ppb at 220 m.

Comparison of O_3 and NO_2 Concentrations between 2010 and 2018

Fig. 7 depicts the time series of O_3 and NO_2 hourly mean concentrations during summer at the same site in Tianjin in different years (2010 and 2018); the observation data in 2010 are available in Ran *et al.* (2012). The measurements in 2010 and 2018 were performed at the same location. O_3 concentrations at both times were measured using UV photometric O_3 analyzers. These analyzers were calibrated using a primary standard UV photometric O_3 calibrator, which is traceable to the standard reference photometer maintained at the World Calibration Centre of the World

Meteorological Organization in EMPA, Switzerland. NO analyzers were operated according to the principles of chemiluminescence. In contrast to the direct measurement process implemented in 2018, that adopted in 2010 involved first converting NO_2 into NO by using a molybdenum converter heated to approximately 325°C and then performing measurements using chemiluminescence. The NO/N_2 standard mixtures for *in situ* calibrations were compared with the same NO standard produced by Scottgas (<https://industry.airliquide.us/scott-gas-mixtures>), which can be traced to the National Institute of Standards and Technology (Lin *et al.*, 2011). NO was converted into NO_2 through gas-phase titration for NO_2 calibration. Therefore, comparison of data from 2010 and 2018 was sound. Because insufficient data prevented meaningful statistical analysis (only 381 hourly overlapping NO observations), NO and NO_x were not compared for these periods.

Compared with the data in 2010, NO_2 concentrations in 2018 were significantly lower, whereas the range of O_3 concentrations was similar but with higher O_3 peaks in 2018. From the statistical data (Table 2 and Fig. S3), hourly mean NO_2 concentration was found to be 15.70 ± 0.27 ppb and the median value was 14.58 ppb in 2018, whereas the hourly mean was 25.51 ± 0.39 ppb and the median was 24.54 ppb in 2010. The difference in NO_2 mean was close to 10 ppb. The average O_3 hourly mean was 39.0 ± 0.9 ppb in 2010 and 47.0 ± 1.0 ppb in 2018, and the O_3 median values were 31.2 ppb in 2010 and 41.0 ppb in 2018, respectively. Even for the lower end of the concentration distribution, O_3 concentration was slightly higher in 2018 than in 2010. For example, O_3 concentration was 24.2 ppb in 2018 and 14.6 ppb in 2010 for 25% of the lowest value.

The comparability of pollutant concentrations in different years depends not only on changes in source emissions but also on weather conditions. The weather influences atmospheric diffusion, transmission, and photochemical reactions, and conditions vary from year to year. During the comparison periods, the average temperatures were 25.7°C

Fig. 7. Time series of O_3 and NO_2 concentrations in different years in urban Tianjin.

in 2010 and 29.5°C in 2018, the average relative humidity (RH) recordings were 64% in 2010 and 67% in 2018, and the average wind speeds were 0.9 m s⁻¹ in 2010 and 1.9 m s⁻¹ in 2018. The prevailing wind was from east in 2018 and from the west and north in 2010. To minimize the effects of meteorological variations, O₃ and NO₂ concentrations from 2010 and 2018 were reclassified and averaged according to temperature, relative humidity, wind speed, and wind direction, as suggested by Lin *et al.* (2012). Thus, the differences were evaluated for various meteorological categories, and the results are shown in Figs. 8 and 9. It is worth noting that less proportions of data could be found in the lowest or the highest values of bins. For example, the frequency of wind speed higher than 3 m s⁻¹ only took up a factor of less than 6% in 2018. Temperatures between 22°C and 35°C comprised 93.5% and 94.4% of the recordings in 2018 and 2010, respectively.

As shown in Fig. 8, the concentration of O₃ increased with temperature; as RH and wind speed increased, O₃ concentration increased and then decreased. The differences between the O₃ concentrations in 2010 and 2018 were noticeable for the RH and wind direction categories, with considerably higher concentrations in 2018 than in 2010. However, the differences were more complex for the temperature and wind speed categories, possibly as a result of the interaction effect of temperature and wind speed. Generally, higher temperature resulted in higher wind speeds, and high wind speed could reduce the ground-level O₃ concentration.

As shown in Fig. 9, the concentration of NO₂ increased

with RH and decreased with the increasing temperature and wind speed. Because limited data were available from 2010 for temperatures higher than 34°C, the concentrations of NO₂ were considerably higher in 2010 than in 2018 for various meteorological categories. Therefore, emission reduction should effectively reduce NO₂ concentrations. This can be confirmed by decreasing tropospheric NO₂ column density in Tianjin since 2010 (You *et al.*, 2016), according to satellite observations, and the decreasing trend observed in routine NO₂ measurements in the 2018 Tianjin Ecology and Environment Statement.

In summary, O₃ concentration during summer in Tianjin increased from 2010 to 2018, whereas NO₂ concentration decreased.

Ozone Production Efficiency

Based on ground measurements, the relationship between O_x (O_x = O₃ + NO₂) and NO_z (NO_z = NO_y - NO_x) was calculated and ozone production efficiency (OPE) was obtained from the slope of the correlation. Fig. 10 depicts the correlation between O_x and NO_z from 11:00 to 16:00 during the observational period. Linear regression was performed using a reduced major axis regression method. A significant correlation was noted at the confidence level of 0.05, and the correlation coefficient (R) was 0.434. From the slope of the correlation, OPE in summer in urban Tianjin was determined to be 6.0 ± 0.4. This value falls within the OPE values measured in other urban areas (Ge *et al.*, 2010).

A lack of measurements of VOCs makes ozone sensitivity difficult to discuss. Previous studies have suggested that O₃

Fig. 8. Mixing ratios of O₃ in 2010 and in 2018 as functions of (a) relative humidity, (b) wind speed, (c) ambient temperature, and (d) wind direction.

Fig. 9. Mixing ratios of NO₂ in 2010 and in 2018 as functions of (a) ambient temperature, (b) relative humidity, (c) wind speed, and (d) wind direction.

Fig. 10. Correlation between O₃ and NO₂ during 11:00–16:00 in summer in urban Tianjin.

is more sensitive to VOCs than to NO_x in Tianjin (Han *et al.*, 2013; Han *et al.*, 2015). On the basis of the present results, we could only conclude that O₃ increased considerably while NO₂ decreased between 2010 and 2018. Lower NO chemical titration can increase the mean concentration of O₃ and reduce its range, although this does not hold for daytime peak O₃. Further work is needed to understand if the changes in the emission of VOCs and the ratio of VOCs to NO_x have caused the increase in surface O₃ concentration.

CONCLUSIONS

An air flow drainage system utilizing a long Teflon pipe was built on a 355-m meteorological tower in urban Tianjin to obtain simultaneous measurements of gaseous pollutants at a high altitude (220 m a.g.l.) and near the surface (3 m a.g.l.) during summer 2018. O₃ loss in the pipeline was tested and found to be negligible, confirming that the instruments installed 3 m above the ground could accurately measure the concentrations of pollutants at 220 m.

Similar variations in the concentrations at 3 m and 220 m were measured for both O₃ and NO_x, but noticeable differences between the two heights during the day and the night. Specifically, the diurnal O₃ concentrations were higher near the surface than at the high altitude, whereas the nocturnal ones displayed the opposite trend. Also, the NO₂ concentrations at 3 m generally exceeded those at 220 m by an amount that was slight during daytime but far more prominent during nighttime. The concentrations of NO were higher near the surface, with the largest and smallest differences between the two altitudes occurring during the day and the night, respectively. Finally, the O₃ concentrations displayed significant diurnal differences but minimal nocturnal ones between the ground and the upper layer.

The concentrations of the O₃ precursor NO_x were higher at 3 m than 220 m, which, along with the much-increased photochemical generation of O₃ (O₃) near ground level during daytime, indicates that the surface O₃ was primarily affected by local photochemical formation during the summer in urban Tianjin. From 07:00 till 14:00, the O₃

concentration increased on average by approximately 50 ppb near the surface and 46 ppb in the upper layer. The measurements collected during summer 2010 reveal that the NO_x concentrations significantly decreased between this period and summer 2018, whereas the O₃ concentrations increased, and the vertical structures for these pollutants also greatly changed from 2006 till 2018. Using field measurements, the summer ozone production efficiency measurement, OPE (O₃/NO₂) was reported as 6.0 ± 0.4 during the summer in urban Tianjin for the first time.

ACKNOWLEDGMENTS

This study was supported by the National Natural Science Foundation Committee of China (Grant No. 91744206) and the Science and Technology Plan of Beijing (Grant No. Z181100005418016).

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <https://doi.org/10.4209/aaqr.2019.10.0505>

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Received for review, October 10, 2019

Revised, March 27, 2020

Accepted, April 8, 2020