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# Ozone concentration at various heights near the surface layer in Shenyang, Northeast China

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Ozone pollution has been growing in the recent decade, becoming a critical urban environmental issue in China. However, Shenyang's near-surface ozone concentration (ground to 100 m altitude) is of grave concern. To obtain the ozone concentration and the corresponding meteorological conditions from 1 October 2018, to 30 September 2019, we built observatory sites at low ( $\approx 15$  m) and high ( $\approx 90$  m) layers in Shenyang, northeast China. Then, we analyzed the temporal variation of ozone concentration and discussed the relationship between ozone concentration and the meteorological factors at low and high layers. Compared with the high layer, the ozone concentration in the low layer is chartered with an earlier peak and higher diurnal range. The ozone concentration in all seasons first peaked at a low-layer height, in early in winter (15:00) and late summer (17:00). Then, the peak at high-layer height lagged for behind 1–2 h, generally occurring between 17:00 and 19:00. The variations in ozone concentration at low and high layers differed in daytime and nighttime. The diurnal ranges of ozone concentrations at the low layer were higher than those at the high layer in the four seasons examined. Overall, ozone concentration correlated significantly with air temperature, having correlation coefficients of 0.814 ( $p < 0.05$ ) in the low layer and 0.731 ( $p < 0.05$ ) in the high layer. Inversely, it showed a weak correlation with relative humidity: 0.310 ( $p < 0.05$ ) and 0.351 ( $p < 0.05$ ) in the low and high layers, respectively. Also, the correlation coefficients with wind speed were meager at both layers. Generally, ozone pollution is not severe in Shenyang.

## KEYWORDS

vertical observation, ozone, meteorological factor, near-surface, correlation

## Introduction

Tropospheric ozone is a critical atmospheric pollutant with a strong oxidizing property. It is also a greenhouse gas without any benefits to animals, plants, or the climate (Liu, 2019; Yu et al., 2021). With the implementation of emission reduction measures in China, particulate matter pollution has reduced (Wang W. X. et al., 2019). In contrast, near-ground ozone concentration has been increasing recently (Cheng et al., 2019; Deng et al., 2022). Furthermore, ozone has become a primary pollutant in some

Chinese cities (Li et al., 2021). Thus, studying ozone is crucial to improving their atmospheric environment.

Previous studies on ozone have mainly focused on the characteristics of spatial and temporal distributions (Wang et al., 2018; Liu et al., 2019b; Oufdou et al., 2021), formation mechanism (Ridel et al., 2014; Wang et al., 2021), chemical precursors (An et al., 2015; Shi et al., 2015; Lyu et al., 2021), influencing factors (Pu et al., 2017; Wang Z. et al., 2019), etc. Generally, ozone concentration has lucid spatial distribution characteristics, i.e., higher in the suburbs and lower in the urban areas (Im et al., 2019). Many studies reported that daily ozone concentration is a unimodal curve change that peaks in the afternoon and plateaus in the morning (Liu, 2019; Han et al., 2021). Also, the concentration is respectively higher and lower in the summer and winter than the average (Zhang and Zhang, 2019; Wang et al., 2020; Zhang et al., 2021). Key factors that influence the seasonal and spatial ozone variations in a specific region include horizontal inflows and outflows via long-range transport, vertical stratospheric-to-tropospheric transport, photochemical production and destruction, and deposition on the Earth's surface (Logan, 1985; Ma et al., 2002). Moreover, most studies were done in temporal and spatial variations.

With improved urbanization, ozone studies on vertical height are gradually increasing. Generally, the tropospheric O<sub>3</sub> increased to around 8 km altitude, and then increased rapidly above 8 km with a larger variability near the tropopause in mid-latitudes (Beekmann et al., 1994; Logan, 1994; Cooper et al., 2005). For PBL, the O<sub>3</sub> concentrations increased sharply below 1 km and then remained fairly constant (~52 ppbv) between 1 and 2 km in Beijing by Airbus In-Service Aircraft (MOZAIC) program (Ding et al., 2008). Using a differential absorption ozone Lidar, He and coworkers (He et al., 2020) found that ozone concentration increases before decreasing with altitude (300–3,000 m), peaking at 600–800 m. Based on the observation at 8, 120, and 280 m layers, the ozone layer was 325 and 255 mm at the Beijing and Tianjin towers, respectively. The daily average ozone concentration increased with altitude from August 18 to 22 September 2006 (Sun et al., 2010). In the vertical direction, few studies on ozone in Shenyang, northeast China focused on the near-surface (0–100 m), predominantly the space for urban activities. Because near-surface ozone pollution is closely related to human health, we monitored the ozone concentration at low (15 m) and high (90 m) layers in Shenyang. This study aims to provide ozone concentration variations at 15 and 90 m and discuss the relationships between ozone and meteorological factors in the study area. *Data and methods* introduces observation data and method. *Results and discussion* presents results that include statistical characteristics of seasonal, monthly and diurnal ozone concentration in this city, and the relationship between ozone concentration and meteorological factors. *Summary and conclusion* summarizes the results.

## Data and method

### Study area and observation instrument

The study area is located in Shenyang, a heavily industrialized city. Based on the seventh population census, Shenyang has a permanent resident population of  $9.03 \times 10^6$  in 2020 (<https://www.maigoo.com/news/585028.html>). The topography is flat, and the altitude is 40–50 m above sea level. It has a humid, warm continental monsoon climate, with a mean temperature of  $-6^{\circ}\text{C}$  in January and  $23^{\circ}\text{C}$  in July. The annual mean precipitation in Shenyang is 716 mm (average from 1951 to 2010), with the precipitation concentrated in summer (June–August).

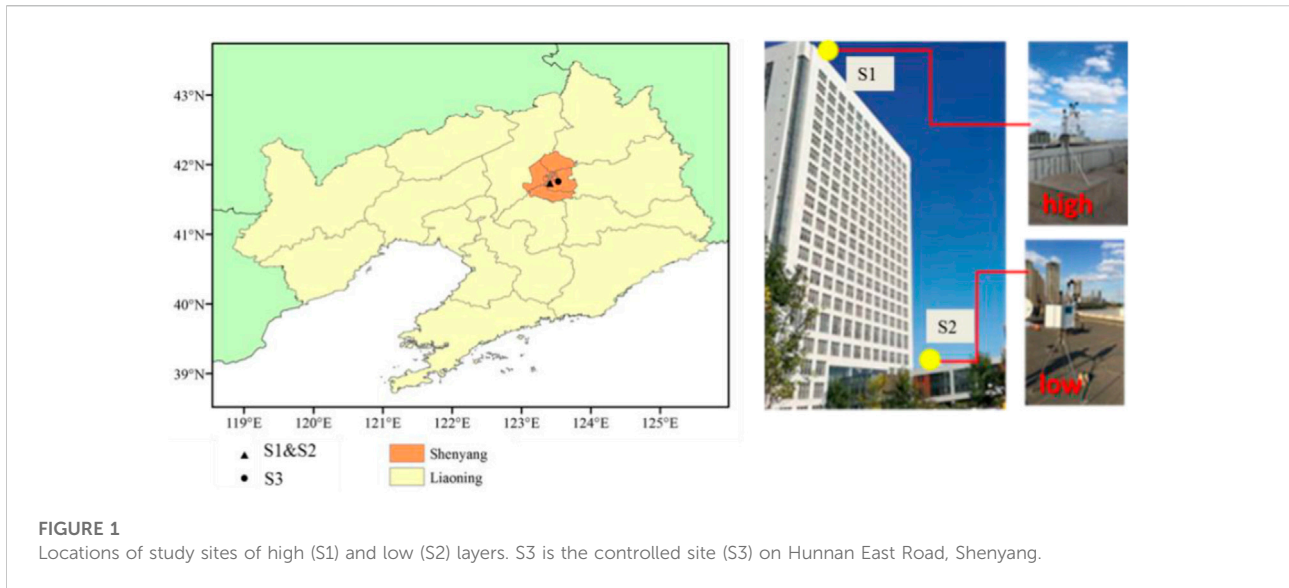
The study site (Figure 1) is in the yard of Shenyang Institute of Atmospheric Environment, China Meteorological Administration. The site is surrounded by a primary school (south), a branch of the Hunhe River (north), a residential area (east), and bare land (west).

The monitoring instrument (H6 air quality early warning system (constant temperature)) produced by Qingdao Hecheng Environmental Protection Technology Co., Ltd., was set on the roof platform of two buildings of different heights (Figure 1). The heights are considered low (30 m) and high (90 m) layers, respectively, influenced by various pollution sources such as industrial pollution, traffic pollution, etc., (China State Bureau of Technical Supervision, 1992).

### Observation data and method

We measured the ozone concentration, air temperature, wind speed, and relative humidity from 1 October 2018, to 30 September 2019. Table 1 lists the description of observed elements. The interval time was 1 min, and the entire data underwent strict quality control, including eliminating outliers and interpolating missing test data. We employed the data from the surrounding site (about 13.5 m below vertical distance and 10 m horizontal distance to the observed site at the low layer) because of missing measurements of meteorological elements at that layer. Also, we compared the daily mean ozone concentration measured in the low layer in this study with those (<http://www.cnemc.cn/>) from the controlled site (S3 in Figure 1) on Hunnan east road of Shenyang. After removing missing data and outliers, 331 sample pairs were obtained from both sites, separated by 5 km. The trend of ozone concentration at both sites in November was similar (Figure 2A), and the correlation coefficient was 0.80 ( $p < 0.01$ ) (Figure 2B). Thus, the observed data can represent the status of ozone in Shenyang.

Furthermore, the spring, summer, autumn, and winter seasons reported here correspond to March–May, June–August, September–November, and December–February. In addition, vertical airflow speed data indicating pollutant

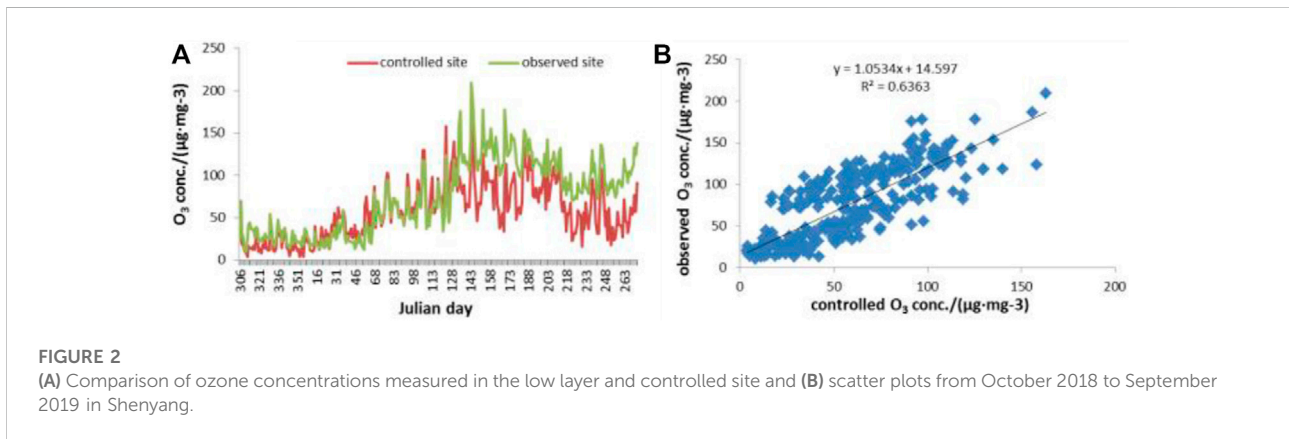


**FIGURE 1**  
Locations of study sites of high (S1) and low (S2) layers. S3 is the controlled site (S3) on Hunnan East Road, Shenyang.

**TABLE 1** Description of monitored ozone concentration and meteorological factors.

Elements	Resolution	Missing data at low/high layer	Interval time (min)
O <sub>3</sub>	0.1 μg•m <sup>-3</sup>	29/0 days	1
Wind speed	0.1 m s <sup>-1</sup>	0/7 days	1
Temperature	0.1°C	37/7 days	1
Relative humidity	0.5%	37/7 days	1

Electrical power failure and instrument failure were responsible for the missing data.



**FIGURE 2**  
(A) Comparison of ozone concentrations measured in the low layer and controlled site and (B) scatter plots from October 2018 to September 2019 in Shenyang.

mixing in the lower boundary layer were from the European Centre for Medium-Range Weather Forecasts (ECMWF). The data had horizontal and vertical resolutions of 0.125 and 25 hPa, respectively.

Shenyang’s mean boundary layer heights in 2018 were calculated using the Weather Research and Forecasting (WRF)

model. Boundary layer height was determined from the MYNN2 PBL scheme (Nakanishi and Niino, 2003) in the WRF model. The scheme used 1.5-theta-increase and Turbulent Kinematic Energy (TKE) methods to define the Planet Boundary Layer Heights (PBLH). The 1.5-theta-increase method defines PBL heights as the level at which the

TABLE 2 Seasonal ozone concentrations ( $\mu\text{g m}^{-3}$ ) in the low and high layers of Shenyang.

Season	Low layer	High layer
Spring	$76.4 \pm 28.21$	$93.23 \pm 26.63$
Summer	$112.76 \pm 28.51$	$104.13 \pm 32.08$
Autumn	$69.79 \pm 33.68$	$53.18 \pm 23.92$
Winter	$24.87 \pm 6.27$	$36.18 \pm 6.64$

potential temperature first exceeds the minimum potential temperature within the boundary layer by 1.5 K. When applied to observed temperatures, this method can produce PBL-height estimates that are unbiased relative to profiler-based estimates (Nielsen-Gammon et al., 2008). However, their study did not include Low-Level Jets (LLJ). Banta et al. (2006) show that a TKE-based threshold is a viable estimate of the PBL heights in LLJs. Therefore, a hybrid definition (a *tanh* weighting function) was implemented using both methods, weighting the TKE-method (Nakanishi and Niino, 2003) more during stable conditions (PBLH < 400 m). In addition, a variable, the TKE threshold (0.02 times the maximum TKE below 250 m), was also used in the TKE methods. The ECMWF data verified the simulated results of PBL heights. Both correlation coefficients reached 0.65 ( $p < 0.05$ ) and passed the *t*-test.

## Results and discussion

### Seasonal and monthly variations of ozone concentrations

Among the four seasons, the ozone concentration was highest in summer with  $112.76 \pm 28.51 \mu\text{g m}^{-3}$  at the low layer and  $104.13 \pm 32.08 \mu\text{g m}^{-3}$  at the high layer. The sequence was summer > spring > autumn > winter (Table 2). Generally, the ozone concentration at the low layer was higher in summer and autumn, while those at the high layer were higher in winter and spring.

The variations in ozone concentration and meteorological elements in low and high layers from October 2018 to September 2019 in Shenyang are shown in Figure 3. For monthly variations (Figure 3A), trends for ozone concentrations at both height layers are similar, having a peak and a valley. The maximum ozone concentrations in both heights occurred in June with  $129.73 \pm 23.51 \mu\text{g m}^{-3}$  in the low layer and  $128.74 \pm 22.01 \mu\text{g m}^{-3}$  in the high layer, while the minimum values were in January with  $22.78 \pm 5.85 \mu\text{g m}^{-3}$  in the low layer and in December with  $32.21 \pm 3.11 \mu\text{g m}^{-3}$  in the high layer, respectively. The ozone concentration peak in the summer relates to meteorological factors, such as high temperature and relative humidity, intense insolation, and transport of Asia summer wind (Liu

et al., 2021). From June to October, the ozone concentration was higher in the low layer than in the high layer, and the maximum difference appeared in October, reaching  $35.60 \mu\text{g m}^{-3}$ . However, from November to May, it is the contrary, with the corresponding maximum difference ( $16.6 \mu\text{g m}^{-3}$ ) occurring in January.

In general, the monthly variations of ozone concentrations are similar in the two height layers (Figures 3A,B). The daily mean ozone concentrations in most months were under  $160 \mu\text{g m}^{-3}$  (limit of ozone pollution standard) except in June, with five and 7 days in the low and high layers, respectively. This result suggests that ozone pollution seldom happens in Shenyang.

The daily mean wind speed, air temperature, and relative humidity in the two layers in Shenyang are shown in Figures 3C–E. Wind speed in the high layer was much higher than in the low layers, with low and high wind speed (LWS and HWS) values of  $0.47$  and  $1.23 \text{ ms}^{-1}$ , respectively. However, air temperatures in the low ( $12.67^\circ\text{C}$ ) and high ( $12.62^\circ\text{C}$ ) layers differed slightly. The same was observed for relative humidity, i.e., 46.68% and 43.22% in low and high layers, respectively). Compared with the two layers, the air temperature was higher in the low layer from May to November, but higher in the high layer from December to March (unmeasured data in the low layer in April). For relative humidity, it was higher in the low layer from October to April, while the opposite occurred from May to September.

Many studies indicated that meteorological factors could influence vertical ozone concentration (Ma et al., 2011; Guo et al., 2013; Dai et al., 2021). Thus, we correlated the ozone levels against the meteorological data to discuss factors influencing ozone pollution (Figure 4). Ozone concentration has a better relationship with air temperature; both correlation coefficients were 0.814 ( $p < 0.05$ ) in the low layer and 0.731 ( $p < 0.05$ ) in the high layer. As for the relative humidity, the respective values were 0.310 ( $p < 0.05$ ) and 0.351 ( $p < 0.05$ ), while the correlation coefficients with wind speed were meager for both layers. It also shows that ozone concentration is well correlated with air temperature but poorly correlated with relative temperature and wind speed in Xi'an (Hu et al., 2021) and Cangzhou (Xiong et al., 2022), China.

### Diurnal characteristics of ozone concentrations

Figure 5 shows the diurnal variation of hourly ozone concentrations. Generally,  $\text{O}_3$  concentration, whose variation is characteristic of photochemical reactions, was low at night, gradually increasing in the morning and peaking at dusk (Xu et al., 2008; Li et al., 2021; Liu et al., 2021). In all seasons, the  $\text{O}_3$  concentration first peaked at the low-layer height in early winter (15:00) and late summer (17:00). Then, the peak at the high layer height lagged for 1–2 h (between 17:00 and 19:00). The diurnal variations (the difference between the maximum and minimum)

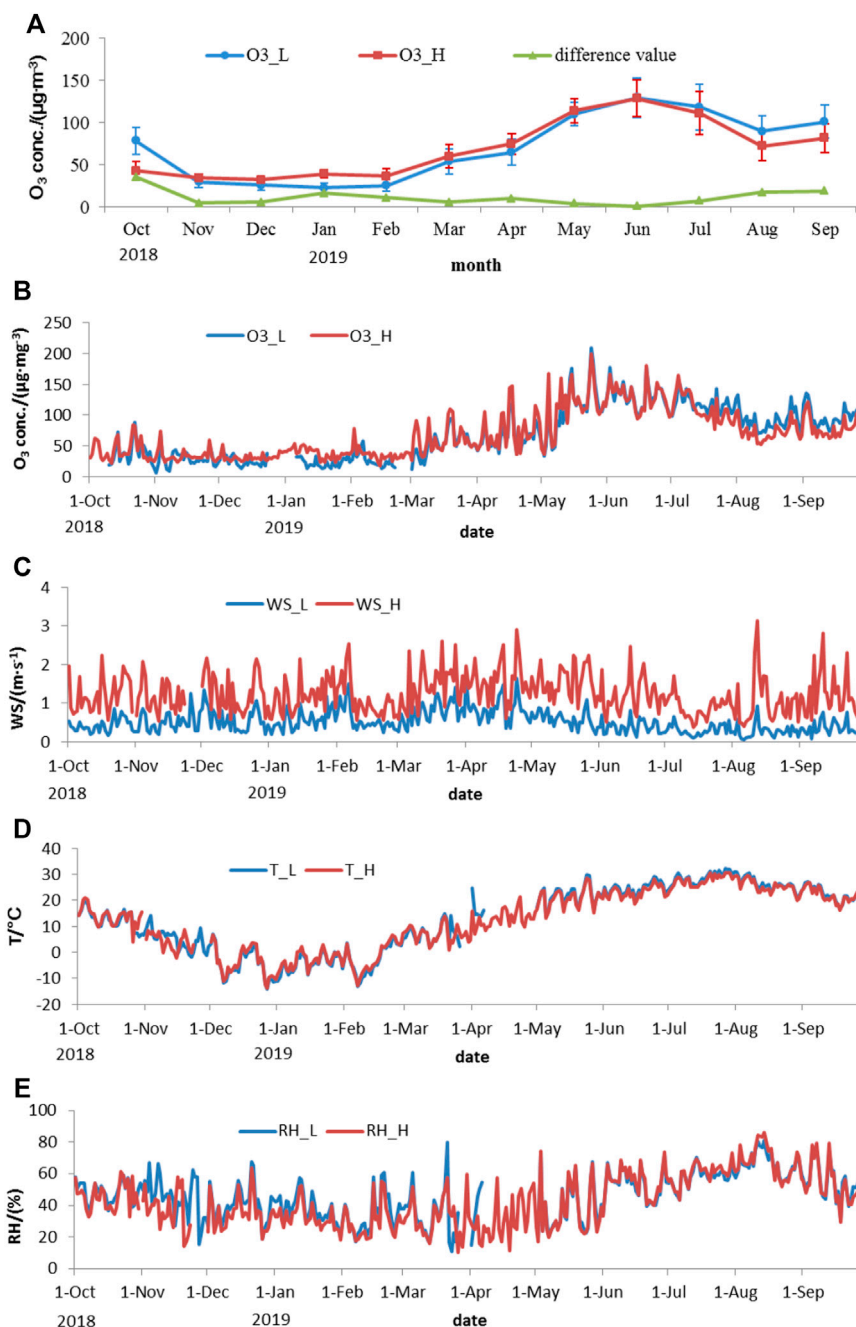


FIGURE 3

Variation in mean (A) daily and (B) monthly ozone concentration and the corresponding (C) wind speed, (D) temperature, and (E) relative humidity in low and high layers from October 2018 to September 2019 in Shenyang, China.

of ozone concentrations at the low layer were 44.70, 67.67, 39.60, and 19.99  $\mu\text{g}\cdot\text{m}^{-3}$  in spring, summer, autumn, and winter, respectively. These values were higher than their counterparts in the high layer. Compared with the high layer, the ozone concentration in the low layer is chartered with an earlier peak and wider diurnal variations. This occurrence could be

attributed to the higher concentrations of ozone precursors in the lower layer, i.e., conducive conditions for ozone formation and transportation of updraft transporting air mass from the low layer, leading to the lags in ozone maximum in the high layer.

In spring, the ozone concentration during the daytime was slightly higher at the low layer than at the high layer. The

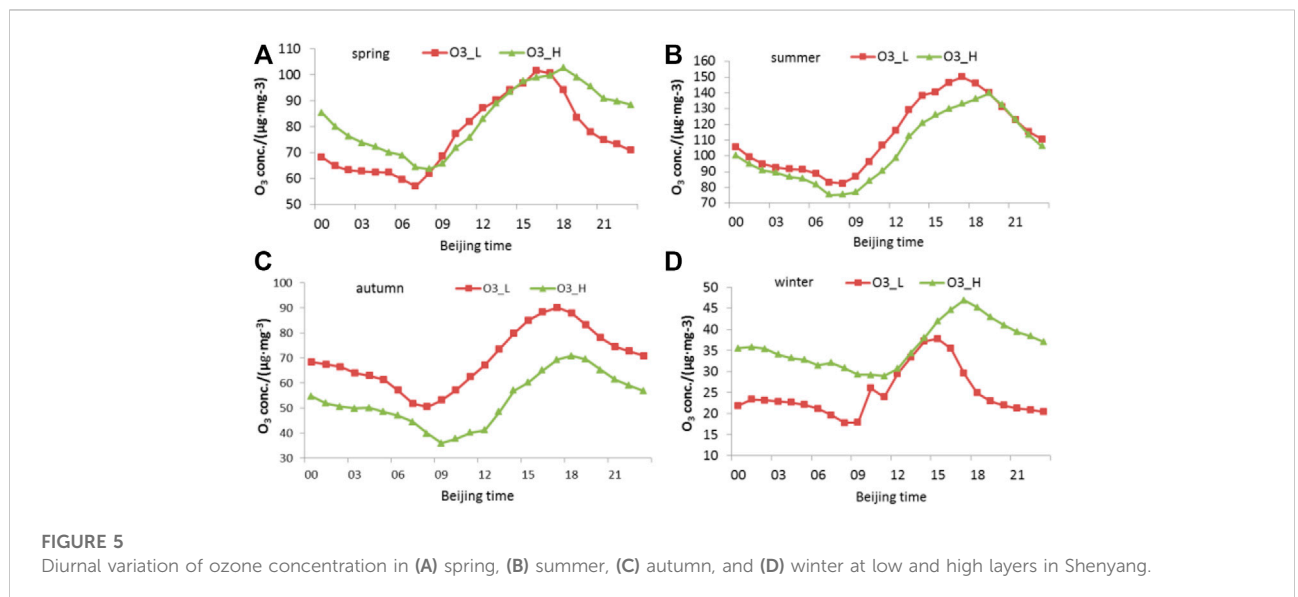
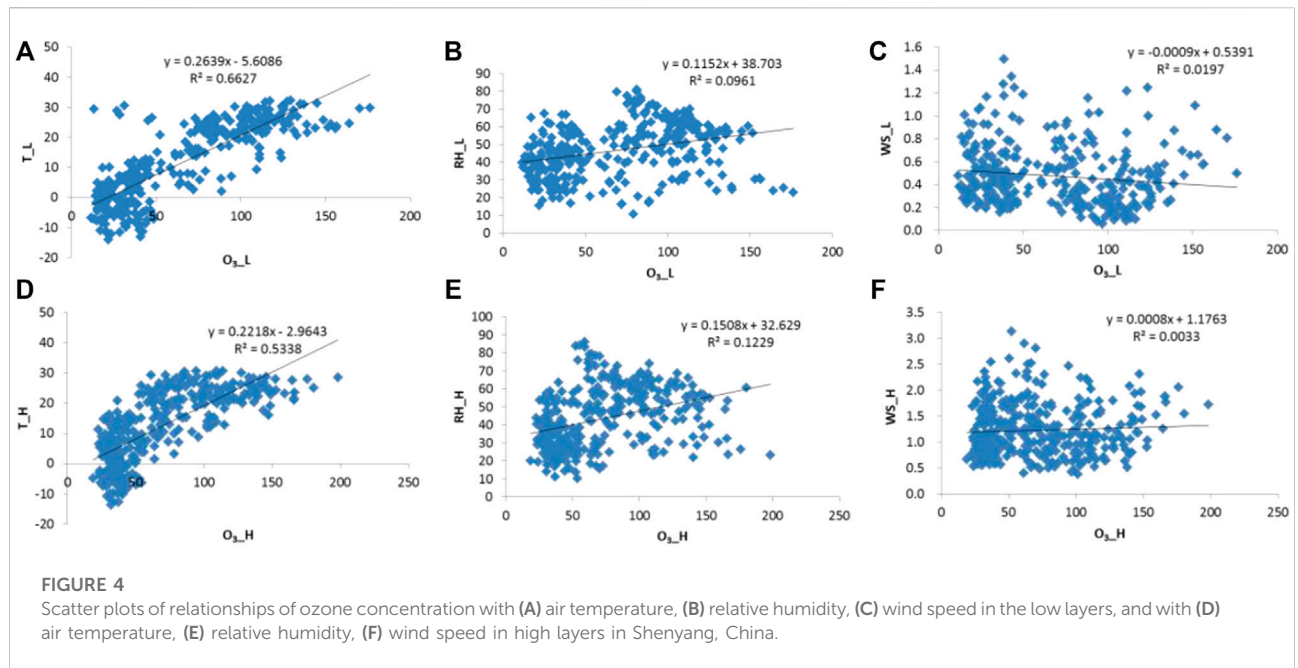
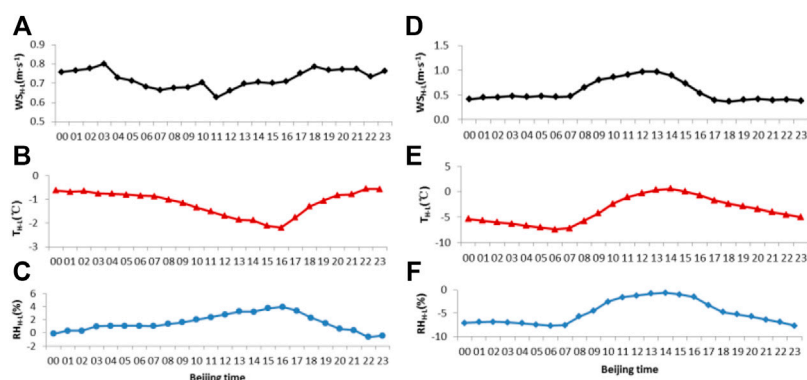


TABLE 3 Atmospheric boundary layer height (m) at Shenyang in 2018.

BTC	Annual average	Spring	Summer	Autumn	Winter
02:00	328.8	319.0	305.3	275.2	414.2
14:00	1,296.2	1,490.0	1,388.0	1,377.5	962.2
Average	672.2	748.2	716.2	644.7	594.1



**FIGURE 6**

Diurnal variation (high minus low) of (A) wind speed, (B) air temperature, (C) relative humidity in summer, and the corresponding values (D–F) in winter in Shenyang.

differences between the two heights were below  $6.17 \mu\text{g m}^{-3}$ , while during the nighttime, it was lower at the low layer than at the high layer, with an increase in the corresponding differences. In the daytime, the boundary layer height in spring was the highest among the four seasons in Shenyang, reaching 1,490 m at 14:00 (Table 3). Numerous ozone photochemical reactions were initiated in the daytime, and the vertical mixing near the ground was intense, resulting in similar ozone concentrations at the two heights during the day. On the other hand, during nighttime, the “titration” consumption of NO was evident in the lower layer due to the high NO concentration. The dry deposition of ozone (Ripperton and Vukovich, 1971) also led to a more significant loss in the lower layers, and the atmospheric turbulence weakened. The vertical mixing at different altitudes was lower during daytime, so the ozone concentration in the lower layer was lower than in the upper layer.

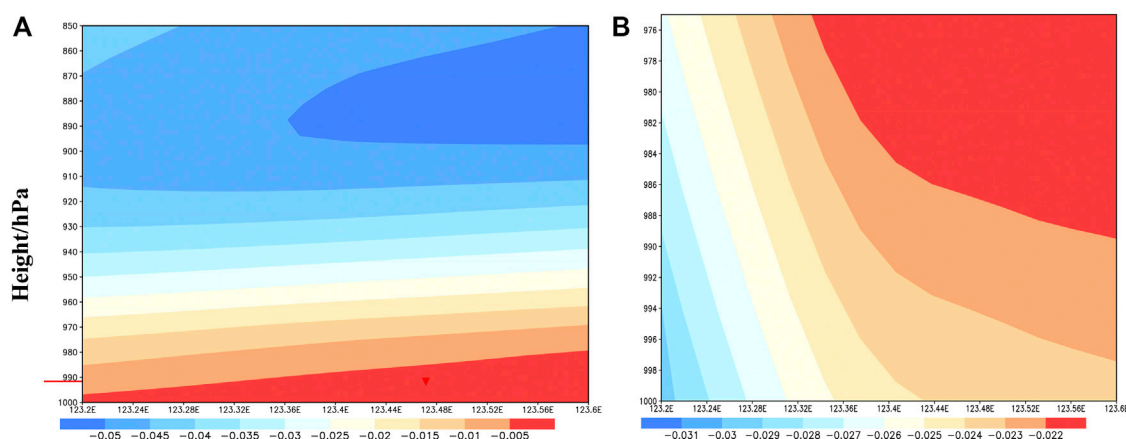
In summer, the ozone concentration was higher at the low layer than at the high layer during daytime and nighttime, while the difference between the two heights was higher in the daytime than at night. The transport of ozone and its precursors by the Asian summer monsoon (ASM) during the day, combined with the intense local photochemical reactions, resulted in a prominent ozone concentration in the lower layer (Liu et al., 2019a). At night, NO transported by ASM and locally emitted NO simultaneously consumed ozone at both heights. More ozone was consumed at the low level than the high level because NO was more concentrated at the low level. Furthermore, vertical mixing in summer, even at night, makes the ozone concentrations similar in both layers.

We analyzed the corresponding meteorological factors in summer at low and high layer heights in Shenyang (Figure 6). Lower air temperature, higher relative humidity, and higher wind speed existed at the high layer height in summer than at the low layer, whose vertical distribution suggests unstable atmosphere stratification (Li et al., 2019). Also, the profile of

the vertical speed of airflow indicated that the area over the observation site ( $123.41^\circ\text{E}$ ,  $41.73^\circ\text{N}$ ) from the ground to 990 hPa (about 100 m) was a weak updraft area (Figure 7A). A typical updraft at 18UTC on 7 July 2018 over Shenyang is shown in Figure 7B, bringing pollutants upward thus shrinking the concentration differences between the low and high layers. All meteorological elements were advantageous to the vertical mixing of pollutants.

Further, the ozone concentration variations in autumn and summer were similar, i.e., higher at the low layer than at the high layer. At the same time, the difference (about  $16 \mu\text{g m}^{-3}$ ) between the two heights was stable throughout the day. Also, the ozone concentration decreased significantly in autumn than in summer, only being  $50.56\text{--}90.16 \mu\text{g m}^{-3}$  in the low layer and  $35.93\text{--}70.86 \mu\text{g m}^{-3}$  in the high layer.

During winter, the ozone concentration was lower at the low layer than at the high layer throughout the day. In contrast, the difference between the two heights was slight in the daytime but significant in the nighttime. An inverse temperature occurred in winter, and wind shear was weaker in winter than in summer, while the horizontal wind speed was also meager (Figure 6D). Under these meteorological conditions, pollutant transport in vertical and horizontal directions was slow (Li et al., 2019). Thus, local photochemical generation and consumption of ozone were more critical. During winter, the ozone concentration was lower in the high layer than in the low layer. And the first reason is as follows: ozone was generated and mixed vertically along the boundary layer during daytime. NO consumed the uniformly mixed ozone at nighttime. The difference in NO consumption by ozone at different heights during nighttime was different. Another reason was that central heating during winter, adopted in Shenyang in recent years, ensured that the total emissions (including NO<sub>x</sub>) from elevated point sources



**FIGURE 7**

Vertical profile of airflow speed (unit: Pa/s, positive value is downdraft; negative value is updraft) along 41.73°N (A) in summer and (B) at 18UTC on 7 July 2018 over Shenyang.

were effectively controlled (Yang et al., 2005). Thus, NO emissions were lesser at the upper layer than at the lower layer. The same was the ozone consumption, resulting in a lower ozone concentration in the lower layer than in the upper layer.

## Summary and conclusion

We monitored ozone concentration and meteorological factors at the low layer ( $\approx 15$  m) and high ( $\approx 90$  m) layer in Shenyang, northeast China. Then, we analyzed the temporal variation of ozone concentration from 1 October 2018, to 30 September 2019. We also discussed the relationships between ozone concentration and meteorological factors (i.e., air temperature, relative humidity, and wind speed).

The ozone concentration in the four seasons peaked at the low layer first, early in winter, and late in summer. The peak at the high layer height lagged for 1–2 h. For spring, the ozone concentration in the daytime was slightly higher at the low layer than at the high layer, with a meager difference between the two heights. Whereas during the nighttime, the concentration was lower at the low layer than at the high layer, with an increased corresponding difference. In summer, the ozone concentration was higher at the low layer than at the high layer throughout the day. The difference between the heights was higher during the day than at night. During autumn, the variation in the ozone concentration was similar to that in summer, while the difference between the heights was stable throughout the day. Finally, in winter, the ozone concentration was lower at the low layer than at the high layer during daytime and nighttime, with some slight difference between the two heights in the daytime but higher at night.

## Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding authors.

## Author contributions

Conceptualization, LL, and NL; methodology, LL, and NL; software, LS, and HW; validation, LL, and XL; formal analysis, LL, XL, and YM; investigation, LL, XL, and YW; resources, LL, NL, and YW; data curation, LL, and HW; writing-original draft preparation, LL, and NL; writing-review and editing, LL, LS, ZZ, HW, XL, YW, NL, and YM; project administration, LL, and YM. All authors have read and agreed to the submitted version of the manuscript.

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study. The English in this document has been checked by two professional editors, both native speakers of English.

## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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