Long-term ozone variability in the vertical structure and integrated column over the North China Plain: results based on ozonesonde and Dobson measurements during 2001–2019

Jinqiang Zhang, Dan Li, Jianchun Bian, Yuejian Xuan, Hongbin Chen, Zhixuan Bai, Xiaowei Wan, Xiangdong Zheng, Xiangao Xia and Daren Lü

Key Laboratory of Middle Atmosphere and Global Environment Observation, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, People’s Republic of China
2 Collaborative Innovation Center on Forecast and Evaluation of Meteorological Disasters, Nanjing University of Information Science and Technology, Nanjing 210044, People’s Republic of China
3 Xianghe Observatory of Whole Atmosphere, Institute of Atmospheric Physics, Chinese Academy of Sciences, Xianghe 065400, People’s Republic of China
4 College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, People’s Republic of China
5 College of Atmospheric Sciences, Lanzhou University, Lanzhou 730000, People’s Republic of China
6 Chinese Academy of Meteorological Sciences, China Meteorological Administration, Beijing 100081, People’s Republic of China
* Authors to whom any correspondence should be addressed.
E-mail: zjq@mail.iap.ac.cn and lidan@mail.iap.ac.cn

Keywords: ozonesonde measurements, vertical ozone structure, total ozone column, long-term variability, North China Plain

Abstract
Ozonesonde launches were routinely performed in Beijing from March 2001 to February 2019 to generate a unique long-term (18 years) vertical ozone profile dataset over mainland China. This study elucidates the vertical ozone structure on various temporal scales during this 18 years period by using the entire ozonesonde data product for the first time. Moreover, the long-term variability in the integrated ozone column over the North China Plain (NCP) is also explored by comparing the retrievals from ozonesonde at the Beijing urban site and a Dobson ozone spectrometer at the Xianghe suburban site. Our results indicate that vertical ozone exhibited clear monthly variability characterized by high values of tropospheric ozone during warm seasons and high values of stratospheric ozone during cold seasons. Stratospheric intrusions frequently occurred during spring and effectively transported cold air masses with high ozone from the lower stratosphere downward into the upper troposphere. Evident interannual variability in the lower troposphere and in ozone-rich areas of the stratosphere was revealed by vertical ozone distributions. The integrated total ozone columns retrieved from ozonesonde and Dobson bear close resemblance and exhibit strong sinusoidal monthly variations. In the troposphere and boundary layer, the integrated ozone column presented a significant positive trend during 2001–2012 in Beijing; a sudden decline occurred between 2011 and 2013, which was followed by a slow and insignificant increase after the implementation of the Clean Air Action plan in 2013 on the NCP.

1. Introduction
Ozone is a major atmospheric component and is significant for human health, ecological balance and climate change (Anenberg et al. 2012, IPCC 2014, Tai et al. 2014). As an important secondary pollutant, ozone in the troposphere is mainly produced in polluted air by photochemical oxidation of nitrogen oxides and volatile organic compounds in the presence of sunlight (Atkinson 2000, Monks et al. 2009).
Plain (NCP), which is one of the most populated and polluted regions in China due to rapid population growth and economic development over the last few decades (Ding et al 2008, Dufour et al 2018, Qin et al 2018, Miao et al 2021). Surface ozone pollution has become even worse since the implementation of the Clean Air Action plan in 2013, when the Chinese government made major efforts to reduce anthropogenic emissions in polluted regions (Li et al 2020, Wang et al 2020) that are highly associated with surface solar variations (Yu et al 2020, 2021).

In contrast to high near-surface ozone levels, which are harmful to humans and living systems, the ozone layer in the stratosphere shields life on Earth by absorbing ultraviolet radiation from the Sun (Gicerone 1987). Approximately 90% of atmospheric ozone resides in the lower and middle stratosphere (between approximately 15 and 35 km altitude), which can affect climate change by influencing the radiative balance of absorption and emission in the longwave region and absorption in the shortwave region (Shindell et al 1999, Cañada et al 2000). Depletion of the stratospheric ozone layer has been recognized as one of the most important environmental issues over the past several decades (Molina and Rowland 1974, Farman et al 1985, Zhou et al 1995). Due to the decreased atmospheric loading of anthropogenic ozone-depleting substances, a recovery of the stratospheric ozone layer has been reported in certain regions (Kuttippurath et al 2018, Chipperfield et al 2017).

Accurate ozone observations are vital to support national and international policy decisions related to ozone pollution near the surface and ozone variability in the stratosphere. As a small, lightweight and compact balloon-borne instrument, electrochemical concentration cell (ECC) technology-based ozonesonde (Komhyr 1969) is an important instrument able to provide in situ vertical ozone profiles with high vertical resolution from the surface to layers at approximately 30–35 km altitude (Thompson et al 2007, Vömel and Diaz 2010). A global network of ozonesonde stations has generated long time series data to support studies on ozone variation on various temporal scales. For example, the average ozone increases have been observed over the last half of the 20th century at northern mid-latitudes (Oltmans et al 2006); however it seems that the rate of increase has more recently slowed, particularly over western and central Europe and less definitively over North America and Japan (Parrish et al 2012). Nair et al (2013) reported that the total column ozone trends was about $0.55 \pm 0.30$ DU yr$^{-1}$ over the period 1997–2010 at Haute–Provence Observatory (43.93° N, 5.71° E), a northern mid-latitude station. Weber et al (2018) indicated that the total ozone levels remained stable in the Northern Hemisphere extratropics (35° N–60° N) over the period 1996–2016. By analyzing ozonesonde measurements in Pohang (36.02° N, 129.23° E), South Korea from 1997 to 2017, Shin et al (2020) suggested that the ozone concentration in the stratospheric layer, tropospheric layer, and total column ozone increased by 0.45%, 5.26%, and 1.07% dec$^{-1}$, respectively. The ozone increase in the lower troposphere was also revealed over the last 2 decades in three subtropical cities (Hong Kong in South China, and Ha Noi and Naha in Japan) in East Asia (Liao et al 2021).

Compared to the other regions of the Earth, such as North America, Europe and Japan mentioned above, the knowledge of long-term vertical ozone variability over China is quite insufficient due to the lack of vertical ozone measurements. To fill this gap, we successively developed the single-cell GPSO3 ozonesonde (Wang et al 2003, Xuan et al 2004) and two half-cell ozonesonde (Zhang et al 2014a) to provide vertical ozone measurements in Beijing from March 2001 to February 2019, resulting in a long-term (18 years) vertical ozone profile dataset over the NCP. As a unique routine measurement once per week in mainland China (Bian et al 2007), our ozonesonde dataset is the best candidate to determine long-term vertical ozone variability over the megacities on the NCP. Although several previous studies have used a part of the dataset to validate satellite measurements and model products (e.g. Bian et al 2007, Wang et al 2012) and explore the regional ozone variability within a certain altitude range (e.g. Zhang et al 2020, Tang et al 2021), further analyses are undoubtedly needed since there is still a lack of studies reporting the long-term vertical ozone variations by using the entire almost 2 decades long dataset, which is also the primary objective of this study. More importantly, this study exhibits vertical ozone variability on various temporal scales (monthly, seasonally and annually) by employing the entire 18 years long quality-controlled ozonesonde data product for the first time. In addition to the ozonesonde observations in Beijing, we also deployed a ground-based Dobson ozone spectrometer to perform total ozone column measurements at Xianghe (WMO 1994)—a suburban site close to Beijing on the NCP. By comparing retrievals from ozonesonde and Dobson at the two sites with different backgrounds, i.e. urban Beijing and suburban Xianghe, the long-term integrated ozone column variations over the NCP are also elucidated in this study. The paper is organized as follows. The sites and measurements are described in section 2. The vertical ozone structure and long-term ozone column variations are presented in sections 3 and 4, respectively, and a conclusion is summarized in section 5.

2. Sites and measurements

The ozonesonde was released from the Beijing Nanjiao Meteorological Observatory (116.47° E, 39.81° N; 31 m above sea level; figure 1), a national
Figure 1. Location of ozonesonde launches in Beijing (red star) and Dobson measurements at Xianghe (blue rectangle).

Figure 1. Location of ozonesonde launches in Beijing (red star) and Dobson measurements at Xianghe (blue rectangle).

A sounding observation station (ID: 54511) of the China Meteorological Administration. The site is located near the South 5th Ring Road and the primary air pollutants are emitted by motor vehicles. The impact by the interference of NO\textsubscript{2} and SO\textsubscript{2} on the ozonesonde measurements in the boundary layer should decrease in recent years since the emissions of the two pollutants have been reduced on the NCP. We normally launch the ozonesonde every Thursday at 14:00 China Standard Time when the maximum surface ozone concentration and mixing layer height generally occur during the day. The single-cell ozonesonde, which is named GPSO\textsubscript{3} and consists of a platinum gauze cathode and an activated carbon anode immersed in neutral potassium iodide solution (Wang et al 2003), was developed at the Institute of Atmospheric Physics (IAP), Chinese Academy of Sciences, and has provided measurements since March 2001. The performance of the GPSO\textsubscript{3} ozonesonde has been evaluated by comparing its profile observations with those from a commercial ECC ozonesonde manufactured by the Vaisala Company, which showed a correlation coefficient of 0.99 (Xuan et al 2004). The relative bias between the GPSO\textsubscript{3} and Vaisala ozonesondes was generally within 10% for the vertical ozone measurements and was about 3% for the total ozone column (Wang et al 2004). The GPSO\textsubscript{3} ozonesonde was launched until January 2013 when an updated two half-cell ozonesonde (simply named ‘IAP ozonesonde’) using 1% KI buffered cathode sensor solutions was developed as a substitute (Zhang et al 2014a). The anode electrode of the GPSO\textsubscript{3} ozonesonde is made by sticking carbon powder together, in which air may exist and explode at low pressure levels and thus affect the detection altitude of ozone profiles (Zheng and Li 2005). The IAP ozonesonde employs a platinum mesh as the electrode in every cell to address this issue (Zhang et al 2014a). A preliminary evaluation showed that the average difference in the ozone partial pressure between the IAP ozonesonde and ECC (model ENSCI-Z) ozonesonde was <0.3 mPa in the troposphere and <1 mPa in the lower stratosphere. The total ozone columns retrieved from the IAP ozonesonde and the surface Brewer spectrophotometer agreed, with a relative difference and correlation coefficient of 6% and 0.94, respectively. The low-pressure pump efficiency, derived from laboratory tests and outdoor comparisons, is ∼1.0 below 100 hPa and increases to 1.17 at 10 hPa and 1.28 at 5 hPa, respectively (Zheng et al 2018). The correction of a pump efficiency profile to all IAP ozonesonde measurements has resulted in a higher detection performance of the ozone profile than our preliminary evaluation results in Zhang et al (2014a).

During the pre-flight procedures, two parameters, i.e. response time and background current which are recognized as indicators to assess the
ozonesonde detection performance, are tested for our ozonesonde. The typical values for these two parameters are less than 30 s and 0.2 μA (Zheng et al 2018), which are consistent with the values of the commercial ECC ozonesonde (such as model ENSCI-Z) widely used across the world. In addition to regular measurement once per week, more frequent ozonesonde launches were made during intensive observational periods, such as almost daily release in June 2013 during an atmospheric ozone-haze observational campaign (Zhang et al 2014b). Data quality control was conducted to the ozonesonde measurements by identifying anomalous values and instrument malfunctioning via an inspection and selection procedure (Liao et al 2021). To reduce the impact by anode electrode explosion in the single-cell ozonesonde, this study further selects an ozone profile with a maximum detection altitude higher than 28 km that generally passes over the ozone peak area in the stratosphere, resulting in a total of 827 ozone profiles analyzed in this study. The ozone columns below the balloon burst height was calculated by integrating the ozone partial pressure from the ozonesonde profile (Tarasick et al 2021). To integrate the total ozone column for the ozonesonde profile above the balloon burst height, satellite-derived ozone climatology is used in this study (McPeters et al 1997). Our ozonesonde is coupled to a CF-06A meteorological radiosonde to provide conventional meteorological parameters, i.e. air pressure, temperature, relative humidity (RH), wind speed and wind direction. The radiosonde showed good performance in the 8th World Meteorological Organization (WMO) International Radiosonde Comparison (Nash et al 2011). A dry bias existed in the RH measurements above the upper troposphere (Bian et al 2011), indicating that the RH measurements at high altitude levels are more suitable for qualitative reference rather than quantitative analysis. Given the close relationships and interactions between ozone and its surrounding atmospheric environment, the vertical temperature and RH profiles are presented in section 3 to aid the understanding of ozone variability.

A ground-based Dobson ozone spectrometer (instrument number: D075), which is calibrated every few years, is deployed to provide total ozone column measurements at Xianghe (116.95° E, 39.75° N; 95 m above sea level; figure 1)—a suburban site on the NCP. Xianghe is a county in Hebei Province and is located between the two megacities of Beijing and Tianjin. The Dobson site, which is located ~60 km east of the ozonesonde location, is surrounded by cropland, densely occupied residences and light industry. Xianghe is an observation station (ID: 208) of the World Ozone Ultraviolet Data Center and has been uploading measurements for data archives since 1979 (WMO 1994). The Dobson measurements on all days available between March 2001 and February 2019 are analyzed in this study.

3. Vertical ozone structure from ozonesonde measurements in Beijing

Figure 2 shows the vertical ozone variability from individual ozonesonde profile and the monthly sample numbers during 2001–2019. Four ozonesonde launches were generally performed every month in Beijing, except for a few months in 2002 when observations were unavailable due to system updates. At a more detailed level, the sample numbers tended to be more intact after 2013 when the double-cell IAP ozonesonde replaced the single-cell GPSO3 ozonesonde. An obvious annual cycle in the ozone variability was presented by individual profile measurements, especially at the boundary layer and lower and middle stratosphere. High near-surface ozone levels were observed by ozonesonde records in the middle of 2004, 2007, 2010 and 2011. The ozone-rich areas were distributed between 20 and 30 km in the stratosphere during the observational periods. Due to the improvement in the quality of balloons and ozonesondes, the maximum detection altitude increased greatly after 2008 and seemed to be more stable and generally higher than 35 km after 2013 when the type of ozonesonde was updated. The occurrence frequency of ozone measurements above 28 km was ~94% for all double-cell IAP ozonesonde launches in Beijing.

The monthly evolution of atmospheric temperature, RH and ozone as well as their average profiles in the four seasons (spring: March–May; summer: June–August; autumn: September–November; winter: December–February) is shown in figure 3. Clear monthly variability was presented by the atmospheric thermal (figure 3(a)) and moisture structure (figure 3(b)), as shown by the elevated thermal tropopause height and warmer air masses containing more water vapor in the troposphere during hot seasons than during other seasons. Relative to the other months, the air mass in the lower stratosphere (15–20 km) was colder from May to October (figure 3(a)) when less ozone content (figure 3(c)) absorbed less radiation to generate a heating effect at that altitude range. Overall, the vertical ozone exhibited strong monthly variations in the troposphere (figure 3(c)), i.e. higher ozone levels in warm months than in the other months due to varying rates of photochemical ozone production induced by various daylight hours, solar zenith angles and atmospheric temperatures on an annual cycle. The peak ozone partial pressure in the troposphere was generally located around the boundary layer in all four seasons, with a maximum of 9.3 mPa at 0.75 km in summer, followed by 6.1 mPa at 1.4 km in spring, 5.3 mPa at 1.5 km in autumn, and 2.7 mPa at 4.1 km in winter (figure 3(f)). The vertical locations of the above four peak ozone levels increased with decreasing near-surface temperature in the four seasons (figure 3(d)). The maximum and lowest-altitude summer peak may
Figure 2. Monthly number of ozonesonde samples (a) and vertical ozone distribution from individual profiles (b) during 2001–2019.

be associated with strong photochemical production, transport of regional pollution, and intense biomass burning activities in summer on the NCP (Ding et al 2008). Notably, consistent with ozone variations, a humidity inversion layer (i.e. humidity increasing with height) was also trapped within the boundary layer (figure 3(e)), indicating a high degree of coupling relationship between ozone and RH in the lower troposphere associated with the near-surface thermal dynamic structure. In the stratosphere, similar peak ozone partial pressures were detected in summer and autumn, i.e. 13.6 mPa at 25.6 km and 13.5 mPa at 25.0 km, respectively. Relative to the above two seasons, larger peak ozone partial pressures located lower in the stratosphere were observed in spring and winter, which were 14.6 mPa at 22.4 km and 15.0 mPa at 22.7 km, respectively.

Previous studies have suggested the transport of ozone-rich stratospheric air into the troposphere due to tropopause folding associated with cut-off low pressure systems over northeastern China and the Tibetan Plateau, which is recognized as a hotspot of deep stratospheric intrusion events (Škerlak et al 2014, Song et al 2016, Li et al 2018). However, this feature has not been well reported on the NCP. As shown in figures 3(a) and (c), our results indicate that stratospheric intrusions generally occurred during the spring season (March–May) and could effectively transport cold air with high ozone concentrations from the lower stratosphere downward into the upper troposphere. Further investigation also revealed that a subpeak with a maximum of 7.8 mPa at approximately 13 km in spring (figure 3(f)) was induced by the tendency of stratospheric intrusions to occur in this season. We also observed the occurrence of stratospheric intrusions in the other seasons besides spring. As an example, figure 4 shows a case study of deep stratospheric intrusion from ozonesonde measurements on 18 June 2013 at 06:00 UTC. The ozone increased up to 7 mPa and RH decreased to nearly zero between 4 km and 7 km above 0 °C level (figure 4(a)). To understand the synoptic background for the ozone enhancement in the middle troposphere, the ECMWF next-generation
Figure 3. Monthly (top panels) and seasonal (bottom panels) distributions of atmospheric temperature (left panels), RH (middle panels) and ozone (right panels) during 2001–2019. The red boxes in panels (a) and (c) note the occurrence of stratospheric intrusions that transport cold air with high ozone concentrations from the lower stratosphere downward into the upper troposphere; the white dash lines in panels (a) and (c) denote the tropopause height. The bottom panels show seasonal variation in spring (green), summer (red), autumn (yellow) and winter (blue); both the temperature (solid line) and potential temperature (dashed line) are presented in figure 3(d).

reanalysis ERA5 data, with a horizontal resolution of 0.25° × 0.25° and a temporal resolution of 1 h, are used to display the synoptic situation at high altitudes (figure 4(b)). The geopotential height at 200 hPa significantly showed a cut-off low pressure system around the northeastern China and an anticyclone around the southwestern China. The Beijing site was located the westerly wind jet between the low pressure and high pressure system. The potential vorticity (PV), usually as a stratospheric tracer, also showed high values within the cut-off low pressure system. The latitude-pressure cross section of potential temperature gradient passing through the Beijing site at 116.5° E displayed a tropopause (two-PVU) fold structure beneath the poleward side of the westerly jet (figure 4(c)). The high potential temperature gradient usually shows a strong static stability in the stratosphere. The fold structure can transport air parcels with high ozone from the stratosphere at the high latitude to the troposphere at the low latitude, which will induce ozone enhancement in the troposphere. The ozone peak structure occurred in the troposphere (figure 4(a)) confirmed that the tropopause fold event contributed to high ozone in the troposphere at Beijing site on the NCP, which is generally similar to the ozone transport mechanism over northeastern China (Li and Bian 2015). As the next step, further statistic analysis will be performed to comprehensively understand the formation mechanism of stratospheric intrusion at the Beijing urban site.

Figure 5 presents the annual vertical distributions of temperature, RH and ozone during 2001–2019 and their average profiles. The tropopause height hovered around a mean magnitude of 11.6 km, and the temperature structure exhibited smooth interannual variations below the tropopause (figure 5(a)). In contrast, larger temperature variability occurred between 15 and 20 km in the lower stratosphere, where colder air masses were detected during 2005–2007 and 2013–2019 compared to the other years. The moisture was generally distributed below the tropopause and demonstrated distinct interannual changes in the lower and middle troposphere (figure 5(b)). Vertical ozone distributions showed great interannual variability; for example, larger ozone content was detected in the lower and upper troposphere between 2005 and
Figure 4. (a) The vertical profiles of ozone (mPa, blue), temperature (°C, red), and RH (%) on 18 June 2013 at 06:00 UTC in Beijing, (b) The PV (shade, PVU), geopotential height (black line, ×10³ gpm), and wind vector (arrow, m s⁻¹) at 200 hPa on 18 June 2013, at 06:00 UTC; the black square marks the Beijing site. (c) Latitude-pressure cross section of potential temperature gradient (shade, K km⁻¹), U-wind (black contour), isentropes (dashed line), and PV (brown line) through Beijing site at 116.5° E; the vertical dashed line marks the Beijing site.

Figure 5. Annual variability in atmospheric temperature (a), RH (b), ozone (c) and their average profiles (d)–(f) during 2001–2019. The white dash lines in panels (a) and (c) denote the tropopause height. The shaded areas in the bottom panels show the annual standard deviations.
2011 relative to the other periods (figure 5(c)). Obvious variations were also presented by ozone-rich areas in the stratosphere, as shown by large ozone levels in 2002, 2008 and 2014 and relatively low ozone levels in approximately 2006. The peak values in the average vertical profiles of humidity and ozone (figures 5(e) and (f)) were 44% and 5.9 mPa, respectively, and both peak values were located at ~1 km, which reflected the atmospheric stratification within the boundary layer. We also found that inversion layers of humidity and ozone were often accompanied or induced by the trap of temperature inversion for the cases study (not shown). However, due to the location variation in the temperature inversion layer, the vertical structure of the temperature inversion was blurred and even invisible (figure 5(d)) in the sea level based climatology (Birner 2006). The formation of temperature inversion generally indicates stable meteorological conditions that are conducive to the occurrence and development of ozone pollution in the boundary layer (Garrido-Perez et al 2019). Previous studies also suggested that high temperature and moderate humidity (Tong et al 2011) and decreased boundary layer height (Haman et al 2014) were in favor of the ozone production and accumulation, which should be related to the co-occurrence of humidity and ozone inversion layers in this study. As mentioned earlier, the stratospheric intrusions induced anomalies in the average ozone (figure 5(f)) and temperature (figure 5(d)) profiles in the upper troposphere. Compared to the ozonesonde measurement in Hong Kong (not shown), a subtropical site in South China, the tropospheric ozone is much higher in Beijing due to the zonal differences between the two sites. Additionally, the anthropogenic polluting emissions at urban Beijing should also favor the ozone production in the boundary layer relative to the clean coastal site.

4. Long-term variability in the integrated ozone column over the NCP

The monthly variability in the total ozone column from the Beijing ozonesonde observations and Xianghe Dobson measurements is shown in figure 6. In general, the retrievals from the two different observational approaches bear close resemblance, both of which exhibited strong monthly variations following a sinusoidal curve shape. The total ozone column increased from January (~350 DU) to a maximum of ~380 DU in March; a decrease was then observed until a minimum of ~305 DU was reached in October, and afterwards, a rapid increase lasted until the end of the year. A finer analysis revealed that the absolute difference between the two retrieval methods was within 6 DU in each month, with a maximum and minimum bias (ozonesonde-Dobson) of 5.9 DU in January and—4.8 DU in April, respectively. The monthly average total ozone column was 340.7 ± 26.3 DU for ozonesonde and 338.9 ± 27.2 DU for Dobson.

The annual variation in the total ozone column is shown in figure 7. A similar variation pattern was generally presented by the two kinds of measurements, although discrepancies could be seen at a more detailed level associated with the ozone spatial variability. As shown by the linear regression analysis, the annual trend of ozonesonde measurements had a negligibly small slope with relatively large uncertainty (0 ± 0.42 DU yr⁻¹), but the slope was not statistically significant because of large interannual fluctuations. Overall, no obvious variation trend was found in the total ozone column in Beijing site, as indicated by a stable total ozone level in the Northern Hemisphere extratropics (Weber et al 2018). Dobson measurements from Xianghe tended to increase before 2010, whereas a decrease followed. An insignificant decreasing trend (−0.41 ± 0.30 DU yr⁻¹) was demonstrated by Dobson measurements during all investigated periods, which was slightly weaker than the decreasing trend (−0.64 DU yr⁻¹) during 1979–2000 (Bian et al 2002). Given the strong seasonal ozone variations (as shown in figure 3), ozonesonde-based annual ozone variability is further investigated according to the four seasons during 2013–2019 since the ozonesonde measurements are incomplete in spring and summer in 2002. As seen in figure 8, distinction existed in ozone trends in the four seasons, with negative trends in summer (−0.77 ± 0.77 DU yr⁻¹) and autumn (−0.47 ± 0.45 DU yr⁻¹) and negligibly small slopes with relatively large uncertainty in the other two seasons. However, the variation trends in the four seasons were statistically insignificant due to large fluctuations, which resulted in an insignificant decreasing annual trends (−0.32 ± 0.49 DU yr⁻¹) for 2013–2019. The seasonal variations in the total ozone column over Beijing may be affected by specific atmospheric dynamics, such as strong convective systems, deep stratospheric intrusion events, and mechanisms associated with cut-off low systems. A more detailed investigation is still required in a follow-up study to establish the relationship between these atmospheric dynamics and seasonal ozone variation in Beijing, such as interesting spring and summer ozone contrast between 2009/2010 and 2013.

To better understand the ozone variability at low altitude levels that are closely related to human activities, figure 9 shows the ozonesonde-based integrated ozone columns in the troposphere (set as below an altitude of 9 km to minimize the stratospheric impact) and boundary layer (below 2 km altitude). The variation pattern was investigated here
Figure 6. Monthly variability and the standard deviations of the total ozone column from the ozonesonde (blue) and Dobson (brown) measurements, with the average values noted in the figure.

Figure 7. Annual variability in the total ozone column measured by ozonesonde in Beijing (blue) and Dobson at Xianghe (brown); the black solid and black dashed lines denote the linear regression of the total ozone column from the two observational methods, with the linear slope and its uncertainty noted in the legend.
by dividing the study period into two shorter periods, i.e. 2001–2012 and 2013–2018, according to the implementation of the Clean Air Action plan in 2013 in China. Ozone presented a positive trend with statistical significance during 2001–2012 at the two altitude ranges, with an increasing rate of \(1.65 \pm 0.43 \text{ DU yr}^{-1}\) and \(0.40 \pm 0.14 \text{ DU yr}^{-1}\) in the troposphere and boundary layer, respectively. A sudden ozone decline was observed in the troposphere between 2011 and 2013, which was suggested being partly associated with less transport of high ozone from the stratosphere to the troposphere during this period (Zhang et al. 2020), despite that stratospheric intrusion was generally not a major ozone source for urban environment settings. Similarly, the ozone decrease also occurred in the boundary layer. A slight surface ozone-negative anomaly was also recorded by the daily maximum 1 h ozone concentration over Beijing during the period (see figure 2 in Cheng et al. 2018), although surface observations may provide limited insight into upper-layer ozone variation trend due to atmospheric variability in vertical thermal dynamic structure (Liao et al. 2021). After the implementation of the Clean Air Action plan in 2013, an insignificantly slow and smooth increase in ozone started, with an increasing rate of \(0.30 \pm 0.16 \text{ DU yr}^{-1}\) and \(0.18 \pm 0.13 \text{ DU yr}^{-1}\) in the troposphere and boundary layer, respectively. The ozone increasing trend in the lower troposphere was also recently reported at the other ozonesonde sites in East Asia, such as at middle latitudes (Shin et al. 2020) and subtropical latitudes (Liao et al. 2021). Despite the consistently positive ozone trend among the sites, we would also like to mention that the ozone spatial variability issue and limitations of the single ozonesonde site to represent a broader region should be well considered for areal analysis of ozone variation trend. Especially given that the ozone spatial variability in the troposphere is highly associated with regional air pollution, even for the two nearby sites on the NCP (Beijing and Xianghe) concerned in this study.

Figure 8. Annual variability in the total ozone column (gray) measured by ozonesonde in spring (a), summer (b), autumn (c) and winter (d); the black dashed lines denote the linear regressions of the total ozone column, with the linear slope and its uncertainty noted in the legend.
5. Summary and conclusions

By using the ozonesondes data in urban Beijing and Dobson measurements at suburban Xianghe, this study quantifies the vertical ozone variability on various temporal scales and elucidates the long-term variability in the integrated ozone column over the NCP. The main conclusions are summarized as follows.

The high ozone partial pressure in the troposphere was generally located around the boundary layer in all four seasons. The ozone-rich areas were distributed between 20 and 30 km in the stratosphere, where similar peak ozone partial pressure was detected in summer and autumn. In contrast, a larger peak ozone partial pressure located lower in the stratosphere was observed in spring and winter. Stratospheric intrusions, which frequently occurred in spring, could effectively transport cold air with high ozone concentrations from the lower stratosphere downward into the upper troposphere, resulting in an ozone subpeak of up to 7.8 mPa at approximately 13 km. The ozonesonde- and Dobson-based total ozone column exhibited consistent and distinct sinusoidal monthly variations, with a maximum of $\sim$380 DU in March and a minimum of $\sim$305 DU in October. No significant variation trend was found in ozonesonde-based total ozone column in Beijing, and an insignificantly decreasing trend ($-0.41 \pm 0.30 \text{ DU yr}^{-1}$) was demonstrated by Dobson measurements at Xianghe. The integrated ozone column increased significantly during 2001–2012 in the troposphere ($1.65 \pm 0.43 \text{ DU yr}^{-1}$) and boundary layer ($0.40 \pm 0.14 \text{ DU yr}^{-1}$) in Beijing. A sudden ozone decline was detected between 2011 and 2013, which was followed by an insignificantly slow and smooth increase after the implementation of the Clean Air Action plan in 2013. In view of the ozone spatial variability and limitations of the single ozonesonde site, long-term ozonesonde measurements at multiple sites are still needed to better understand the near-surface ozone pollution and stratospheric ozone variability on the NCP.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
Acknowledgments

The authors, especially the PIs of the ozonesonde data in Beijing—Yuejian Xuan (xyj@mail.iap.ac.cn) and Jinqiang Zhang (zjq@mail.iap.ac.cn) who developed the ozonesonde and took charge of its launches, appreciate the Beijing Nanjiao Meteorological Observatory for assisting in the ozonesonde launches. We extend thanks to the Xianghe Observatory of Whole Atmosphere for providing ground-based Dobson measurements. We also thank two anonymous reviewers for suggestions that helped improve the paper. This work was supported by the National Key Research and Development Program of China (Grant Nos. 2018YFC1505703 and 2017YFA0603504), the National Natural Science Foundation of China (Grant Nos. 41875183 and 91837311) and the National Basic Research Program of China (Grant No. 2010CB428600).

ORCID ID

Dan Li https://orcid.org/0000-0002-4812-5000

References

Anenberg S C et al 2012 Global air quality and health co-benefits of mitigating near-term climate change through methane and black carbon emission controls Environ. Health Perspect. 120 831–9
Atkinson R 2000 Atmospheric chemistry of VOCs and NOx Atmos. Environ. 34 2063–101
Bian J, Chen H, Vömel H, Duan Y, Xuan Y and Lü D 2011 Intercomparison of humidity and temperature sensors: GTS1, Vaisala RS80, and CPH Adv. Atmos. Sci. 28 139–46
Bian J, Chen H, Zhao Y and Lü D 2002 Variation features of total atmospheric ozone in Beijing and Kunming based on Dobson and TOMS data Adv. Atmos. Sci. 19 279–86
Bian J, Gettelman A, Chen H and Pan L 2007 Validation of satellite ozone profile retrievals using Beijing ozonesonde data J. Geophys. Res. 112 D06305
Birner T 2006 Fine-scale structure of the extratropical tropopause region J. Geophys. Res. 111 D04104
Cañada J, Pedrós G, López A and Boscá J 2000 Influences of the clearness index for the whole spectrum and of the relative optical air mass on UV solar irradiance for two locations in the Mediterranean area, Valencia and Cordoba J. Geophys. Res. 105 4759–66
Cheng N, Chen Z, Sun F, Sun R, Dong X, Xie X and Xu C 2018 Ground ozone concentrations over Beijing from 2004 to 2015: variation patterns, indicative precursors and effects of emission-reduction Environ. Pollut. 237 262–74
Chipperfield M, Bekki S, Dhomse S, Harris N R P, Hassler B, Hossaini R, Steinbrecht W, Thubelmont R and Weber M 2017 Detecting recovery of the stratospheric ozone layer Nature 549 211–8
Cicerone R J 1987 Changes in stratospheric ozone Science 237 35–41
Ding A J, Wang T, Thouret V, Cammas J-P and Nedelec P 2008 Tropospheric ozone climatology over Beijing: analysis of aircraft data from the MOZAIK program Atmos. Chem. Phys. 8 1–13
Dufour G et al 2018 Lower tropospheric ozone over the North China Plain: variability and trends revealed by IASI satellite observations for 2008–2016 Atmos. Chem. Phys. 18 16439–59
Farman J C, Gardiner B G and Shanklin J D 1985 Large losses of total ozone in Antarctic spring reveal seasonal ClOx/NOx interaction Nature 315 207–10
Garrrido-Perez J, Ordóñez C, García-Herrera R and Schnell J 2019 The differing impact of air stagnation on summer ozone across Europe Atmos. Environ. 219 117062
Hamam C, Couzo E, Flynn J, Vizuete W, Heffron B and Lefer B 2014 Relationship between boundary layer heights and growth rates with ground-level ozone in Houston, TX J. Geophys. Res. Atmos. 119 6230–45
IPCC 2014 Climate Change: Synthesis Report. Contribution of Working Groups I, II and III to the 5th Assessment Report of the Intergovernmental Panel on Climate Change ed IPCC, R K Pachauri and L A Meyer (Geneva: IPCC) p 151
Komhyr W D 1969 Electrochemical concentration cells for gas analysis Annu. Geophys. 25 203–10
Kuttippurath J, Kumar P, Nair P J and Pandey P C 2018 Emergence of ozone recovery evidenced by reduction in the occurrence of Antarctic ozone loss saturation npj Clim. Atmos. Sci. 1 42
Li D and Bian J 2015 Observation of a summer tropopause fold by ozonesonde at Changchun, China: comparison with reanalysis and model simulation Adv. Atmos. Sci. 32 1354–64
Li D, Vogel B, Müller R, Bian J, Günther G, Li Q, Zhang J, Bai Z, Vömel H and Riese M 2018 High tropospheric ozone in Lhasa within the Asian summer monsoon anticyclone 2013: influence of convective transport and stratospheric intrusions Atmos. Chem. Phys. 18 17979–94
Li K, Jacob D J, Liao H, Zhu J, Shah V, Shen L, Bates K, Zhang Q and Zhai S 2020 A two-pollutant strategy for improving ozone and particulate air quality in China Nat. Geosci. 12 906–10
Liao Z et al 2021 Tropospheric ozone variability over Hong Kong based on recent 20 years (2000–2019) ozonesonde observation J. Geophys. Res. 126 e2020JD033054
Lin J-T, Wuebbles D J and Liang X-Z 2008 Effects of intercontinental transport on surface ozone over the United States: present and future assessment with a global model Geophys. Res. Lett. 35 L08820
McPeters R D, Labow G J and Johnson B J 1997 A satellite derived ozone climatology for balloonsonde estimation of total column ozone J. Geophys. Res. 102 8875–85
Miao Y, Che H, Zhang X and Liu S 2021 Relationship between summertime concurring PM2.5 and O3 pollution and boundary layer height differs between Beijing and Shanghai, China Environ. Pollut. 268 115775
Molina M and Rowland F 1974 Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone Nature 249 810–2
Monks P et al 2009 Atmospheric composition change—global and regional air quality Atmos. Environ. 43 3268–350
Nair P J et al 2013 Ozone trends derived from the total column and vertical profiles at a northern mid-latitude station Atmos. Chem. Phys. 13 10373–84
Nash J, Oakley T, Vömel H and Li W 2011 WMO intercomparison of high quality radiosonde systems (Yangjiang) Tech. Rep. WMO, WMO/TD-No. 1580, instruments and observing methods report No. 107 (available at: http://library.wmo.int/pmb_ged/wmo_td_1580.pdf) (12 July–3 August 2010)
Neu J L, Flury T, Manney G L, Livesey N J and Worden J 2014 Tropospheric ozone variations governed by changes in stratospheric circulation Nat. Geosci. 7 340–4
Oltmans S J et al 2006 Long-term changes in tropospheric ozone Atmos. Environ. 40 3156–73
Parrish D J et al 2012 Long-term changes in lower tropospheric baseline ozone concentrations at northern mid-latitudes Atmos. Chem. Phys. 12 11485–504
Qin W, Liu Y, Wang L, Lin A, Xia X, Che H, Bilal M and Zhang M 2018 Characteristic and driving factors of aerosol optical depth over mainland China during 1980–2017 Remote Sens. 10 1064
Shin D, Song S, Ryoo S-B and Lee S-S 2020 Variations in ozone concentration over the mid-latitude region revealed by ozonesonde observations in Pohang, South Korea Atmosphere 11 746
Shindell D, Rind D, Balachandran N, Lean J and Lonergan P 1999 Solar cycle variability, ozone, and climate Science 284 305–8
Škerlak B, Sprenger M and Wernli H 2014 A global climatology of stratosphere–troposphere exchange using the ERA-interim data set from 1979 to 2011 Atmos. Chem. Phys. 14 913–37
Song Y, Li D, Li Q, Bian J, Wu X and Li D 2016 The impact of cut-off lows on ozone in the upper troposphere and lower stratosphere over Changchun from ozonesonde observations Adv. Atmos. Sci. 33 155–30
Tai A P K, Martin M V and Heald C L 2014 Threat to future global food security from climate change and ozone air pollution Nat. Clim. Change 4 817–21
Tang G et al 2021 Bypassing the NOX titration trap in ozone pollution control in Beijing Atmos. Res. 249 105333
Tarasick D W et al 2021 Improving ECC ozonesonde data quality: assessment of current methods and outstanding issues Earth Space Sci. 8 e2019EA000914
Thompson A M et al 2007 Intercontinental chemical transport experiment ozonesonde network study (IONS) 2004: 2. Tropospheric ozone budgets and variability over northeastern North America J. Geophys. Res. 112 D12S13
Tong N, Leung D and Liu C 2011 A review on ozone evolution and its relationship with boundary layer characteristics in urban environments Waste Air Soil Pollut. 214 13–36
Vömel H and Diaz K 2010 Ozone sonde cell current measurements and implications for observations of near-zero ozone concentrations in the tropical upper troposphere Atmos. Meas. Tech. 3 495–505
Wang G C, Kong Q X, Xuan Y J, Wan X W, Chen H B and Ma S Q 2003 Development and application of ozonesonde system in China Adv. Earth Sci. 18 471–5 (in Chinese with English abstract)
Wang G C, Kong Q X, Xuan Y J, Wan X W, Chen H B, Ma S Q and Zhao Q 2004 Preliminary analysis on parallel comparison of GPSO3 and Vaisala ozonesondes J. Appl. Meteorol. Sci. 15 672–80 (in Chinese with English abstract)
Wang Y et al 2020 Contrasting trends of PM2.5 and surface-ozone concentrations in China from 2013 to 2017 Natl Sci. Rev. 7 1331–9
Wang Y, Konopka P, Liu Y, Chen H, Müller R, Pflöger F, Riese M, Cai Z and Lü D 2012 Tropospheric ozone trend over Beijing from 2002–2010: ozonesonde measurements and modeling analysis Atmos. Chem. Phys. 12 8389–99
Weber M, Coldewey-Egbers M, Fioletov V E, Frith S M, Wild J D, Burrows J P, Long C S and Loyola D 2018 Total ozone trends from 1979 to 2016 derived from five merged observational datasets—the emergence into ozone recovery Atmos. Chem. Phys. 18 2097–117
WMO 1994 Scientific assessment of ozone depletion: global ozone research and monitoring project Geneva, Switzerland, WMO rep. 37
Xuan Y J, Ma S Q, Chen H B, Wang G C, Kong Q X, Zhao Q and Wan X W 2004 Intercomparisons of GPSOs and Vaisala ECC ozone sondes Plateau Meteorol. 23 394–9 (in Chinese with English abstract)
Young P J et al 2013 Pre-industrial to end 21st century projections of tropospheric ozone from the atmospheric chemistry and climate model intercomparison project (ACCMIP) Atmos. Chem. Phys. 13 3063–90
Yu L, Zhang M, Wang L, Lu Y and Li J 2021 Effects of aerosols and water vapour on spatial-temporal variations of the clear-sky surface solar radiation in China Atmos. Res. 248 1051
Yu L, Zhang M, Wang L, Qin W, Lu Y and Li J 2020 Clear-sky solar radiation changes over arid and semi-arid areas in China and their determining factors during 2001–2015 Atmos. Environ. 223 117198
Zhang J, Xuan Y, Yan X, Liu M, Tian H, Xia X, Pang I and Zheng X 2014a Development and preliminary evaluation of a double-cell ozonesonde Adv. Atmos. Sci. 31 938–47
Zhang J, Yue-Jian X, Xiang-Ao X, Ming-Yuan L, Xiao-Lu Y, Li P, Zhi-Xuan B and Xiao-Wei W 2014b Performance evaluation of a self-developed ozonesonde and its application in an intensive observational campaign Atmos. Ocean. Sci. Lett. 7 175–9
Zhang Y, Tao M, Zhang J, Liu Y, Chen H, Cai Z and Konopka P 2020 Long-term variations in ozone levels in the troposphere and lower stratosphere over Beijing: observations and model simulations Atmos. Chem. Phys. 20 13343–54
Zheng X and Li W 2005 Analysis of the data quality observed by the ozonesonde system made in China J. Appl. Meteorol. Sci. 16 608–18 (in Chinese with English abstract)
Zheng X, Xuan Y, Lin W, Yang J, Tian H, Zhang J and Xing Y 2018 Performance tests and outdoor comparison observations of domestic remade ECC ozonesondes J. Appl. Meteorol. Sci. 29 460–73 (in Chinese with English abstract)
Zhou X, Luo C, Li W and Shi J 1995 Variation of total ozone over China and the Tibetan Plateau low center Chin. Sci. Bull. 40 1396–8