Composited analyses of the chemical and physical characteristics of co-polluted days by ozone and PM$_{2.5}$ over 2013-2020 in the Beijing–Tianjin–Hebei region

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Abstract.

The co-polluted days by ozone (O$_3$) and PM$_{2.5}$ (particulate matter with an aerodynamic equivalent diameter of 2.5 µm or less) (O$_3$&PM$_{2.5}$PD) were frequently observed in the Beijing–Tianjin–Hebei (BTH) region in warm seasons (April-October) of 2013-2020. We applied the 3-D global chemical transport model (GEOS-Chem) to investigate the chemical and physical characteristics of O$_3$&PM$_{2.5}$PD by composited analyses of such days that were captured by both the observations and the model. Model results showed that, when O$_3$&PM$_{2.5}$PD occurred, the concentrations of hydroxyl radical and total oxidant, sulfur oxidation ratio, and nitrogen oxidation ratio were all high, and the concentrations of sulfate at the surface were the highest among all aerosol species. We also found unique features in vertical distributions of aerosols during O$_3$&PM$_{2.5}$PD; concentrations of PM$_{2.5}$ decreased with altitude near the surface but remained stable at 975-819 hPa. Process analyses showed that secondary aerosols (nitrate, ammonium and sulfate) had strong chemical productions at 913-819 hPa, which were then transported downward, resulting in the quite uniform vertical profiles at 975-819 hPa in O$_3$&PM$_{2.5}$PD. The weather patterns for O$_3$&PM$_{2.5}$PD were characterized by a high pressure ridge of the Western Pacific Subtropical High at 850 hPa. The strong southerlies at 850 hPa brought moist air from the south, resulting in a high RH and hence the strong chemical productions around this layer in O$_3$&PM$_{2.5}$PD. The physical and chemical characteristics of O$_3$&PM$_{2.5}$PD are quite different from those of polluted days by either O$_3$ alone or PM$_{2.5}$ alone, which have important implications for air quality management.

Keywords: Co-occurrence, Ozone and PM$_{2.5}$, Pollution, Meteorological parameters.
1. Introduction

Surface ozone (O\textsubscript{3}) and PM\textsubscript{2.5} (particulate matter with an aerodynamic equivalent diameter of 2.5 micrometers or less) are important air pollutants in the atmosphere that have harmful effects on public health (Gao and Ji, 2018; Jiang et al., 2019), ecosystems (Ren et al., 2011; Yue et al., 2017), and crops (Wang et al., 2005; Wang et al., 2007). Surface O\textsubscript{3} is a secondary pollutant produced by photochemical oxidation of volatile organic compounds (VOCs) and nitrogen oxides (NO\textsubscript{x} = NO+NO\textsubscript{2}) in the presence of intense ultraviolet light, and the major PM\textsubscript{2.5} components (nitrate (NO\textsubscript{3}\textsuperscript{-}), ammonium (NH\textsubscript{4}\textsuperscript{+}), sulfate (SO\textsubscript{4}\textsuperscript{2-}), black carbon (BC), organic carbon (OC)) are caused by anthropogenic emissions of aerosols and aerosol precursors. Although surface O\textsubscript{3} and PM\textsubscript{2.5} have different formation mechanisms, they are coupled through the common precursors (NO\textsubscript{x} and VOCs) and photochemical reactions (Chu et al., 2020). Since 2013, stringent clean air actions have been implemented to improve air quality in China (State Council of the People's Republic of China, 2013, 2018). However, O\textsubscript{3} concentrations increased unexpectedly, while PM\textsubscript{2.5} concentrations decreased drastically in the past years (Li et al., 2019). The co-polluted days by O\textsubscript{3} and PM\textsubscript{2.5} (concentrations of both O\textsubscript{3} and PM\textsubscript{2.5} exceed the national air quality standards on the same day, hereafter referred to as O\textsubscript{3}\&PM\textsubscript{2.5}PD) were also reported (Dai et al., 2019). Therefore, it is fundamental to examine the chemical and physical characteristics of O\textsubscript{3}\&PM\textsubscript{2.5}PD.

The Beijing–Tianjin–Hebei (BTH) region is the most populated region in northern China. In the past few years, concentrations of O\textsubscript{3} and PM\textsubscript{2.5} in the BTH were among the highest in China. The Observations from China National Environmental Monitoring Center (CNEMC) showed that the mean and maximum MDA8 (daily maximum 8-h average) O\textsubscript{3} in North China in summer of 2019 were 83 ppb and 129 ppb, respectively, and the summer mean MDA8 O\textsubscript{3} increased with a trend of 3.3 ppb a\textsuperscript{-1} over 2013–2019.
Gong et al. (2020) reported that O$_3$ polluted days (i.e., MDA8 O$_3$ concentration exceeds 80 ppb) in May-July in the BTH increased from 35 days in the year of 2014 to 56 days in 2018. As for observed PM$_{2.5}$, the concentration averaged over BTH had a decreasing trend of 10 μg m$^{-3}$ yr$^{-1}$ over 2013-2019, and the mean value was 79 ± 17 μg m$^{-3}$ over these years (Li et al., 2020). BTH also had the highest frequency and intensity of severe haze pollution days (i.e., days with daily mean PM$_{2.5}$ concentration exceeding 150 μg m$^{-3}$) in China from 2013 to 2017, with an observed mean frequency of 21.2 d yr$^{-1}$ and an observed mean intensity of 231.6 μg m$^{-3}$ (Dang and Liao, 2019).

The interactions between O$_3$ and PM$_{2.5}$ have been reported in previous studies. Zhu et al. (2019) examined the spatial-temporal characteristics of the correlations between observed O$_3$ and PM$_{2.5}$ at 1497 sites in China for 2016 and found that O$_3$–PM$_{2.5}$ had the highest positive correlations (correlation coefficients > +0.7) in July in southern China and the largest negative correlations (r values < −0.5) during January in northern China. Li et al. (2019) used the GEOS-Chem model to analyze the O$_3$-PM$_{2.5}$ relationship in northern China and found that O$_3$ production was suppressed under high PM$_{2.5}$ conditions (PM$_{2.5}$ concentrations > 60 μg m$^{-3}$) because of the reactive uptake of hydrogen oxide radicals (HO$_x$) by aerosol particles. Chu et al. (2020) analyzed the observed daily PM$_{2.5}$ and O$_3$ concentrations in 114 cities in China during years of 2013-2018 and found that the correlations between O$_3$ and PM$_{2.5}$ tended to change from negative in 2013 to positive in 2018 in China as air quality improved.

Few previous studies have examined the co-occurrence of O$_3$ and PM$_{2.5}$ pollution (MDA8 O$_3$ > 80 ppb and PM$_{2.5}$ > 75 μg m$^{-3}$). Zong et al. (2021) used the obliquely rotated principal component analysis in the T-mode (T-PCA) method to identify the synoptic weather pattern associated with O$_3$&PM$_{2.5}$PD in eastern China during
summer of 2015–2018, and found that O₃&PM₂.₅PD were associated with a stable western Pacific subtropical high ridge, which brought warm and moist air flow from the East China Sea to the eastern China to promote hygroscopic growth of fine particulate matter in BTH and northern YRD. Dai et al. (2021) analyzed O₃&PM₂.₅PD in the YRD for April-October of 2013-2019 by using observations and reported that the co-polluted days occurred mainly in April (29.6% of co-polluted days occurred in April), May (23.0%), June (19.5%), and October (10.8%) under meteorological conditions of higher relative humidity, higher surface air temperature, and lower wind speed relative to the days with O₃ pollution alone. Qin et al. (2021) investigated O₃&PM₂.₅PD by using the hourly observed concentrations of water-soluble ions, OC, and elemental carbon (EC) in 2019 in cities of Nanjing and Changzhou. They found that inorganic aerosols mainly existed as NH₄NO₃ and the correlation coefficients between the secondary components NO₃⁻, NH₄⁺, and SO₄²⁻ were relatively high during O₃&PM₂.₅PD in 2019, indicating a significant formation of secondary inorganic aerosols. Although these studies have discussed the meteorological conditions and some chemical characteristics of O₃&PM₂.₅PD, the understanding of O₃&PM₂.₅PD was quite limited because of the limited observations of chemical species involved.

In this work, we take advantage of the comprehensive chemical mechanism of the global chemical transport model to have better understanding of O₃&PM₂.₅PD. We apply the 3-D global chemical transport model (GEOS-Chem) to simulate O₃&PM₂.₅PD in BTH in years of 2013-2020, and investigate the chemical and physical characteristics of O₃&PM₂.₅PD by composited analyses of such days that are captured by both the observations and the model. The objectives of this study are: 1) to examine the underlying chemical mechanisms for O₃&PM₂.₅PD in BTH for warm seasons (April-October) of 2013-2020 by comparing O₃&PM₂.₅PD with polluted days...
by O3 alone or by PM2.5 alone, and 2) to identify the weather patterns that are associated with O3 & PM2.5 PD in BTH. The observations, the reanalyzed meteorological data, the GEOS-Chem model, and the process analysis are described in Section 2. The observed O3 & PM2.5 PD are presented in Section 3.1. The evaluation of simulated concentrations of O3 and PM2.5 as well as the simulated pollution days by O3 and/or PM2.5 are shown in Section 3.2. The underlying mechanisms of O3 & PM2.5 PD are shown in Section 3.3. In Section 3.4, the meteorological conditions for the co-occurrence of O3 and PM2.5 pollution are investigated. The conclusions are presented in Section 4.

2. Methods

2.1 Observed O3 and PM2.5 concentrations

Hourly concentrations of PM2.5 and O3 in China over the years of 2013-2020 were taken from the public website of CNEMC (https://air.cnemc.cn:18007/, CNEMC, 2022). To ensure data quality, the daily mean PM2.5 concentration was calculated when there were valid data for more than 20 h during that day and the MDA8 O3 concentration was calculated when there were valid data for at least 6 h for each 8 h. For the calculation of monthly and annual mean concentrations, the number of days with valid concentrations had to be more than 15 in each month. The spatial distribution of the 79 valid sites within BTH (37-41°N, 114-118°E, the black rectangle) is shown in Fig. 1. For model evaluation, the observed concentrations were averaged over sites within each of the 0.5° latitude × 0.625° longitude MERRA-2 grid cell. There are 18 model grids in BTH. Note that the observed O3 concentrations from this network have a unit of μg m⁻³. For the consistency of observed and simulated O3 concentrations, 1 μg m⁻³ of O3 is approximately 0.5 ppb under the
conditions of 298 K and 1013 hPa. The observed \( \text{O}_3 \) concentrations reported by the CNEMC were under standard conditions of 273 K and 1013 hPa before 31 August 2018 and were under standard conditions of 298 K and 1013 hPa afterwards (http://www.mee.gov.cn/xxgk2018/xxgk/xxgk01/201808/t20180815_629602.html), which were accounted for as \( \text{O}_3 \) concentrations were converted to ppb.

According to the National Ambient Air Quality Standard of China (GB3095-2012), \( \text{O}_3 \) (PM\(_{2.5}\)) concentration exceeds the national air quality standard if the MDA8 \( \text{O}_3 \) (daily mean PM\(_{2.5}\)) concentration is higher than 160 \( \mu \text{g m}^{-3} \) (75 \( \mu \text{g m}^{-3} \)). In this study, we define \( \text{O}_3 \) polluted days (hereafter called ‘\( \text{O}_3\)PD’) for days with MDA8 \( \text{O}_3 \) concentration > 160 \( \mu \text{g m}^{-3} \), PM\(_{2.5}\) polluted days (hereafter called ‘\( \text{PM}_{2.5}\)PD’) with daily mean PM\(_{2.5}\) concentration > 75 \( \mu \text{g m}^{-3} \), and the co-pollution days by \( \text{O}_3 \) and PM\(_{2.5}\) (\( \text{O}_3\&\text{PM}_{2.5}\)PD) with daily MDA8 \( \text{O}_3 \) concentration > 160 \( \mu \text{g m}^{-3} \) as well as the daily mean PM\(_{2.5}\) concentration > 75 \( \mu \text{g m}^{-3} \).

### 2.2 Reanalyzed meteorological fields

Meteorological fields were obtained from the Version 2 of Modern Era Retrospective-analysis for Research and Application (MERRA2), which were generated by the NASA Global Modeling and Assimilation Office (GMAO). The MERRA2 data have a horizontal resolution of 0.5° latitude \( \times \) 0.625° longitude and 72 vertical layers (Molod et al., 2015). To analyze the meteorological conditions for \( \text{O}_3\&\text{PM}_{2.5}\)PD, vertical pressure velocity (OMEGA), planetary boundary layer height (PBLH), temperature (T), relative humidity (RH), surface incoming shortwave flux (SWGDN) are used. Note that the temporal resolution for PBLH, T, and SWGDN is 1h, and that for OMEGA and RH is 3h. Daily mean geopotential heights at 850 and 500 hPa from the National Center for Environmental Prediction (NCEP) and National
Center for Atmospheric Research (NCAR) global reanalysis with a resolution of 2.5° latitude by 2.5° longitude are also utilized in this study.

2.3 Observed aerosol optical depth

We obtained the version 3 datasets of observed daily aerosol optical depth (AOD) of level 2 (improved cloud screened and quality-assured) from Aerosol Robotic Network (AERONET, https://aeronet.gsfc.nasa.gov/new_web/index.html) established by NASA and LOA-PHOTONS (Giles et al., 2019). Three sites in the BTH region have observations available over 2013-2020, including Beijing (39.97°N, 116.38°E), Beijing-CAMS (39.93°N, 116.31°E), and Xianghe (39.75°N, 116.96°E). The AOD values at 440 nm and 675 nm at these three sites are analyzed in this study.

2.4 GEOS-Chem model

We simulated O₃ and PM₂.₅ using the nested version of the 3-D global chemical transport model (GEOS-Chem, version 11-01) driven by the MERRA2 meteorological data. The nested domain was set over Asia (60°-150°E,11°S-55°N) with a horizontal resolution of 0.5° latitude × 0.625° longitude, and the chemical boundary conditions were provided by the global GEOS-Chem simulation with 2.5° latitude × 2.5° longitude horizontal resolution.

The GEOS-Chem model includes fully coupled O₃-NOₓ-hydrocarbon and aerosol chemistry mechanism (Bey et al., 2001; Pye et al., 2009) to simulate aerosols including SO₄²⁻ (Park et al., 2004), NO₃⁻ (Pye et al., 2009), NH₄⁺, BC and OC (Park et al., 2003), mineral dust (Fairlie et al., 2007), and sea salt (Alexander et al., 2005) as well as the gas-phase pollutants such as NOₓ and O₃. Over the Asian domain, the
anthropogenic emissions of OC, BC, carbon monoxide (CO), sulfur dioxide (SO2), NOx, ammonia (NH3), and VOCs were obtained from the Multi-resolution Emission Inventory for China (MEIC), which includes emissions from industry, power, residential and transportation sectors for years of 2014-2017 (Li et al., 2017; Zheng et al., 2018), 2019 and 2020 (Zheng et al., 2021). Emissions in 2018 were obtained by the interpolation of those in 2017 and 2019 for each grid due to the lack of publicly accessible emission inventories for that year. The biogenic emissions in GEOS-Chem are simulated using MEGAN v2.1 (Guenther et al., 2012).

The hourly O3 and PM2.5 concentrations for the years of 2013-2020 were simulated by the GEOS-Chem model which were driven by MERRA-2 meteorological fields. The model was spinne up for 6 months before the integration over the studied time period.

2.5 Process analysis

Process analysis (PA) was applied to identify the relative importance of atmospheric processes in O3&PM2.5PD. PA has been widely used in previous studies to examine the key processes contributing to air pollution episodes (Gonçalves et al., 2009; Dang and Liao, 2019; Gong and Liao, 2019) as well as the interannual and decadal variations of air pollutants (Mu and Liao, 2014; Lou et al., 2015). Five major processes that influence O3 and PM2.5 concentrations were diagnosed at every time step, including net chemical production, dry deposition, horizontal advection, vertical advection, and diffusion, for the regional pollution days (days with more than half of the sites in BTH experiencing pollutions). We carried out PA for O3SPD (exclude O3&PM2.5PD from O3PD), PM2.5SPD (exclude O3&PM2.5PD from PM2.5PD), and O3&PM2.5PD over BTH.
3. Results

3.1 Observed polluted days by O$_3$ and PM$_{2.5}$

Figure 1a shows the spatial distributions of observed numbers of O$_3$PD, PM$_{2.5}$PD, and O$_3$&PM$_{2.5}$PD summed over the warm seasons (April-October) of 2013-2020. The spatial distributions of polluted days in each year are shown in Fig. S1. The numbers of O$_3$PD, PM$_{2.5}$PD, and O$_3$&PM$_{2.5}$PD were high in BTH, which were, respectively, 524.3 344.6, and 128.1 days from observations, as the values were averaged over all sites in BTH. The high numbers of O$_3$PD, PM$_{2.5}$PD, and O$_3$&PM$_{2.5}$PD in BTH were associated with the highest anthropogenic emissions (NO$_x$ and NMVOCs) in this region (Dang et al., 2021).

Figure 1b shows the numbers of days averaged over all sites in BTH for non-polluted days (NPD, MDA8 O$_3$ < 80 ppb and PM$_{2.5}$ < 75 μg m$^{-3}$), O$_3$PD, O$_3$&PM$_{2.5}$PD, and PM$_{2.5}$PD in each month of warm seasons from 2013 to 2020. O$_3$PD and O$_3$&PM$_{2.5}$PD mainly occurred in May, June, and July, while PM$_{2.5}$PD mainly appeared in April and October. The monthly numbers of O$_3$&PM$_{2.5}$PD (PM$_{2.5}$PD) declined from 2013 to 2020, with the fastest drop in June, from 7.5 (17.1) days in June 2013 to 1.8 (1.8) days in June 2020. On the contrary, the numbers of O$_3$PD kept increasing, especially in June, from 10.9 days in June 2013 to 23.6 days in June 2020. The reductions in O$_3$&PM$_{2.5}$PD were associated with the large reductions in PM$_{2.5}$ since the implementation of the Clean Air Action in 2013.
Figure 1. (a) Spatial distributions of observed numbers of O$_3$PD, PM$_{2.5}$PD, and O$_3$&PM$_{2.5}$PD summed over April-October of 2013-2020. The solid black rectangle indicates the BTH region. (b) The observed numbers of NPD (non-polluted days, green), O$_3$PD (blue + purple with slashes), O$_3$&PM$_{2.5}$PD (purple with slashes), and PM$_{2.5}$PD (pink + purple with slashes) averaged over all sites in BTH from April to October in 2013 to 2020.

Figure 2a shows the linear trends of observed O$_3$PD, PM$_{2.5}$PD, and O$_3$&PM$_{2.5}$PD in warm seasons of 2013-2020 averaged over the BTH. O$_3$PD showed an upward trend of 7.9 days yr$^{-1}$ from 2013 to 2020. However, the numbers of PM$_{2.5}$PD and O$_3$&PM$_{2.5}$PD decreased over 2013-2020, with linear trends of -11.2 and -3.4 days yr$^{-1}$, respectively. Figure 2b shows the changes in percentage of O$_3$&PM$_{2.5}$PD in PM$_{2.5}$PD from 2013 to 2020 for each month. It should be noted that, when PM$_{2.5}$PD occurred, the proportions of O$_3$&PM$_{2.5}$PD had an upward trend from 2013 to 2020. In May, June, August, and September of 2020, the proportions of O$_3$&PM$_{2.5}$PD in PM$_{2.5}$PD reached 100%, indicating that PM$_{2.5}$ pollution was accompanied by O$_3$ pollution in
recent years.

**Figure 2.** (a) The trends of observed O$_3$PD, PM$_{2.5}$PD, and O$_3$&PM$_{2.5}$PD in warm seasons from 2013 to 2020 averaged over all sites in BTH. The blue, yellow and purple solid lines (dashed lines) represent the numbers (liner trend) of O$_3$PD, PM$_{2.5}$PD, and O$_3$&PM$_{2.5}$PD, respectively. (b) The percentage of O$_3$&PM$_{2.5}$PD in PM$_{2.5}$PD for April to October in 2013 to 2020. The polluted days were averaged over all sites in BTH.

### 3.2 Simulated polluted days and model evaluation

#### 3.2.1 Simulated surface-layer MDA8 O$_3$ and PM$_{2.5}$ concentrations

Figures 3a and 3b show, respectively, the spatial distributions of simulated and observed surface-layer concentrations of MDA8 O$_3$ and PM$_{2.5}$ in China, as the concentrations are averaged over the warm seasons (April-October) of 2013-2020. The concentrations of MDA8 O$_3$ and PM$_{2.5}$ were both high in BTH. Averaged over BTH and the studied time period, the observed concentrations of MDA8 O$_3$ and PM$_{2.5}$ were 58.1 ppb and 60.3 μg m$^{-3}$, respectively, while the simulated values were 68.0 ppb and 61.1 μg m$^{-3}$, respectively. Figures 3c and 3d compare the time series of observed and simulated daily MDA8 O$_3$ and PM$_{2.5}$ concentrations averaged over the BTH. The simulated daily concentrations of MDA8 O$_3$ (PM$_{2.5}$) in eight warm seasons have a normalized mean bias (NMB) of 7.9% (10.6%). The model generally captures the daily variations (peaks and troughs) in the observed MDA8 O$_3$ and PM$_{2.5}$
concentrations, with R values of 0.80 and 0.72, respectively.

Figure 3. Spatial distributions of simulated (shades) and observed (CNEMC, dots) surface-layer concentrations of (a) MDA8 O$_3$ (ppb) and (b) PM$_{2.5}$ ($\mu$g m$^{-3}$) averaged over the eight warm seasons (April to October, 2013–2020). The solid black rectangle in (a) and (b) indicates the BTH region. Simulated and observed daily concentrations of surface-layer (c) MDA8 O$_3$ and (d) PM$_{2.5}$ averaged over BTH. The correlation coefficient (R) and normalized mean bias (NMB) are also shown for (c) and (d).

NMB = \left(\frac{\sum_{i=1}^{N}(M_i - O_i)}{\sum_{i=1}^{N} O_i}\right) \times 100\%, \text{ where } O_i \text{ and } M_i \text{ are the observed and simulated concentrations, respectively, } i \text{ refers to the } i^{th} \text{ day, and } N \text{ is the total number of days.}

3.2.2 Simulated O$_3$PD, PM$_{2.5}$PD, and O$_3$&PM$_{2.5}$PD

Figure S2 shows the capability of the model in capturing the polluted days. Although the GEOS-Chem model well reproduces the spatial distributions of observed MDA8 O$_3$ and PM$_{2.5}$ concentrations, it underestimates the numbers of O$_3$PD, PM$_{2.5}$PD, and O$_3$&PM$_{2.5}$PD because of the model’s deficiency in capturing the peak
concentrations of air pollutants. Such deficiency was also reported in previous studies that used the GEOS-Chem model or the weather Research and Forecasting with Chemistry (WFR-chem) model (Zhang et al., 2016; Ni et al., 2018; Gong and Liao, 2019; Dang and Liao, 2019). Therefore, to identify O$_3$PD, PM$_{2.5}$PD, and O$_3$&PM$_{2.5}$PD using model results, we utilized lower thresholds by considering the NMBs of simulated MDA8 O$_3$ and PM$_{2.5}$ concentrations in each of 18 grids of BTH. Taking the grid of Beijing as an example, simulated MDA8 O$_3$ and PM$_{2.5}$ had NMBs of -22.0% and -26.9%, respectively, as the simulated concentrations were compared with observations for days with observed concentrations higher than the national air quality standards over the warm seasons of 2013-2020. We then adjusted the threshold of O$_3$PD in this grid to be 62.4 ppb (80 ppb x 78%) and that of PM$_{2.5}$PD to be 54.8 μg m$^{-3}$ (75 μg m$^{-3}$ x 73.1%). These adjusted thresholds were also used to identify O$_3$&PM$_{2.5}$PD. Such approach was also used in previous studies to better capture the pollution events based on the simulations (Dang and Liao, 2019; Gong and Liao, 2019). With the adjusted thresholds, 56-93% of the observed O$_3$PD, PM$_{2.5}$PD, and O$_3$&PM$_{2.5}$PD can be captured by the model (Fig. S2e).

3.2.3 Simulated O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD

Since O$_3$PD or PM$_{2.5}$PD encompasses O$_3$&PM$_{2.5}$PD, we further define O$_3$ single pollution days (hereafter called “O$_3$SPD”, which is to exclude O$_3$&PM$_{2.5}$PD from O$_3$PD) and PM$_{2.5}$ single pollution days (hereafter called “PM$_{2.5}$SPD”, which is to exclude O$_3$&PM$_{2.5}$PD from PM$_{2.5}$PD) for the purpose of obtaining the characteristics of different polluted days. Figures 4a and 4b show, respectively, the spatial distributions of numbers of O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD from observations and from the GEOS-Chem model using the adjusted thresholds. Considering the total of polluted days in 18 grids in BTH, observed O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD were,
respectively, 3937, 3698, and 2024 days, in which 75.0% (2954/3937), 58.1% (2148/3698), and 79.7% (1614/2024) were captured by observation and simulation simultaneously (Fig. 4c). In addition, the numbers of observed and captured $O_3$ SPD, PM$_{2.5}$ SPD, and $O_3$&PM$_{2.5}$ PD in each month are shown in Fig. S3. The model has a fairly good capability of capturing the observed polluted days in each month.

**Figure 4.** Spatial distributions of (a) observed numbers of $O_3$ SPD, PM$_{2.5}$ SPD, and $O_3$&PM$_{2.5}$ PD, (b) numbers of polluted days that were observed and also captured by the GEOS-Chem model with adjusted thresholds, and (c) percentages of observed polluted days that were captured by the model with adjusted thresholds. The values were calculated for the warm months (April to October) of 2013-2020.

### 3.3 Chemical characteristics of polluted days by $O_3$ and PM$_{2.5}$
3.3.1 Atmospheric oxidants of O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD

Figure 5 shows the boxplots of daily concentrations of hydroxyl radical (OH) and total oxidant (O$_x$ = O$_3$ + NO$_2$) from the model for days of O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD that were observed and also captured by the model (samples in Fig. 4b) in the warm seasons of 2013-2020 in 18 grids of BTH. The levels of OH and O$_x$ characterize the atmospheric oxidation capacity, following Hu et al. (2020) and Chan et al. (2017). The concentrations of OH were the highest in O$_3$SPD, with an averaged value of 2.8×10$^6$ molec cm$^{-3}$, followed by that in O$_3$&PM$_{2.5}$PD (2.0×10$^6$ molec cm$^{-3}$) and in PM$_{2.5}$SPD (1.0×10$^6$ molec cm$^{-3}$). Due to the lack of publicly accessible observations of OH in BTH, we compare the simulated OH concentrations with observations reported in the literature. The simulated OH concentrations agree closely with the observed values. In Wangdu of BTH, while the observed daily maximum OH concentrations in summer of 2014 were in the range of 5-15×10$^6$ molec cm$^{-3}$ (Tan et al., 2016), the simulated OH concentrations in the same time period in this work were 3.7-9.5×10$^6$ molec cm$^{-3}$. In Beijing in summer of 2017, the observed daily mean OH concentration was 5.8×10$^6$ molec cm$^{-3}$ (Woodward et al., 2020) and our simulated value was 2.4×10$^6$ molec cm$^{-3}$.

The mean values of O$_x$ were, respectively, 178.7, 118.1, and 184.1 μg m$^{-3}$ in O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD, indicating that the atmospheric oxidation capacity was strong in O$_3$&PM$_{2.5}$PD, which favored the production of secondary components of PM$_{2.5}$. Figure 5 also shows sulfur oxidation ratio (SOR, n-SO$_4^{2-}$/ (n-SO$_4^{2-}$ + n-SO$_2$), where n-SO$_4^{2-}$ and n-SO$_2$ are the concentrations of SO$_4^{2-}$ and SO$_2$, respectively) and nitrogen oxidation ratio (NOR, n-NO$_3$ / (n-NO$_3$ + n-NO$_2$), where n-NO$_3$ and n-NO$_2$ are the concentrations of NO$_3$ and NO$_2$, respectively). SOR and NOR are measures of the conversion degrees of sulfur and nitrogen, respectively (Zhu et al.,
In O₃SPD, PM₂.₅SPD, and O₃&PM₂.₅PD, the averaged values of SOR were 50.0%, 36.7%, and 49.7%, and those of NOR were 55.4%, 70.0%, and 70.2%, respectively. The high SOR and NOR in O₃&PM₂.₅PD indicated the strong formation of SO₄²⁻ and NO₃⁻ that were promoted by high atmospheric oxidation capacity. The monthly variations of OH, Oₓ, and SOR were similar (Fig. 5), with the highest values in summer, owing to the high temperature that promoted high concentrations of oxidants and SOR. It is interesting that SOR and Oₓ values were higher in O₃&PM₂.₅PD than in O₃SPD or in PM₂.₅SPD during May-August. Similarly, NOR values were higher in O₃&PM₂.₅PD than in O₃SPD or in PM₂.₅SPD in May and July-September. Overall, the O₃&PM₂.₅PD occurred with high levels of atmospheric oxidants, SOR, and NOR, leading to combined increases in O₃ and PM₂.₅ concentrations.

**Figure 5.** The boxplots of surface-layer hydroxyl radical (OH, molec cm⁻³), total oxidant (Oₓ, μg m⁻³), sulfur oxidation ratio (SOR, %), nitrogen oxidation ratio (NOR, %) for model-captured O₃SPD, PM₂.₅SPD, and O₃&PM₂.₅PD in 18 grids of BTH in the months of April to October from 2013 to 2020. The whiskers represent the standard deviation, the black line represents the mean value of the samples.

**3.3.2 Surface-layer concentrations of PM₂.₅ components in O₃SPD, PM₂.₅SPD, and O₃&PM₂.₅PD**
The simulated concentrations of PM$_{2.5}$ components (NO$_3^-$, NH$_4^+$, SO$_4^{2-}$, BC, and OC, averaged over 18 grids of BTH are shown in Fig. 6 for days of O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD in the warm seasons of 2013-2020 that were observed and also captured by the model. While the mean concentrations of NO$_3^-$, NH$_4^+$, BC, and OC, were all the highest in PM$_{2.5}$SPD, SO$_4^{2-}$ concentration was the highest in O$_3$&PM$_{2.5}$PD. In O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD, the mean concentrations of SO$_4^{2-}$ were 6.2, 9.4, and 11.97 μg m$^{-3}$, respectively, and the percentages of SO$_4^{2-}$ in PM$_{2.5}$ were 14.9%, 9.0%, and 15.0%, respectively. In July and August, the concentrations of SO$_4^{2-}$ and MDA8 O$_3$ in O$_3$&PM$_{2.5}$PD were the highest compared with those in O$_3$SPD and PM$_{2.5}$SPD (Fig. S4).

**Figure 6.** The concentrations of PM$_{2.5}$ components (μg m$^{-3}$) and percentages of PM$_{2.5}$ components (%) at the surface for NO$_3^-$, NH$_4^+$, SO$_4^{2-}$, BC, and OC. The values were averaged over the model-captured O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD in the months of April to October of 2013-2020 in BTH.

Figure 7 presents the hourly concentrations of NO$_3^-$, NH$_4^+$, SO$_4^{2-}$, BC, OC, and O$_3$ for model-captured O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD over all 18 grids of BTH in
the warm seasons from 2013-2020. Concentrations of NO$_3^-$ and NH$_4^+$ had similarities in diurnal variations, all of which reached the highest values in the early morning (5:00 local time (LT) in O$_3$SPD and O$_3$&PM$_{2.5}$PD, 7:00-8:00 LT in PM$_{2.5}$SPD) and had the lowest values in the late afternoon (18:00 LT in O$_3$SPD and O$_3$&PM$_{2.5}$PD, 16:00 LT in PM$_{2.5}$SPD). Concentrations of BC and OC peaked at the same time as those of NO$_3^-$ and NH$_4^+$ and had the lowest values at 15:00 LT in O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD. The diurnal variations in NO$_3^-$, NH$_4^+$, BC, OC reflected the diurnal variations in PBLH (shown in Fig. S5), which generally reached their highest concentrations before the sudden uplift of PBLH in the early morning (times for uplift of PBLH: 6:00 LT in O$_3$SPD and O$_3$&PM$_{2.5}$PD, 7:00 LT in PM$_{2.5}$SPD ). Compared to O$_3$SPD and O$_3$&PM$_{2.5}$PD, the PBLH of PM$_{2.5}$SPD was lower and uplifted one hour later, which was more favorable for the accumulation of aerosols. During the daytime, PBLH in O$_3$&PM$_{2.5}$PD was between O$_3$SPD and PM$_{2.5}$SPD.

It is worth noting that the diurnal variations of SO$_4^{2-}$ were different from those of other aerosol species, with the highest values at 20:00, 9:00, and 16:00 LT in O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD, respectively, and the lowest values in early morning and night (5:00 LT in O$_3$SPD and O$_3$&PM$_{2.5}$PD, 23:00 LT in PM$_{2.5}$SPD). For the diurnal variation of O$_3$, the highest values occurred during the daytime (16:00 LT in O$_3$SPD and O$_3$&PM$_{2.5}$PD, 15:00 LT in PM$_{2.5}$SPD) and the lowest values appeared at 5:00 LT in all the cases. Therefore, in O$_3$&PM$_{2.5}$PD, the time of the highest value of SO$_4^{2-}$ was the same as that of O$_3$, indicating that SO$_4^{2-}$ and O$_3$ were produced synergistically during the daytime with strong atmospheric oxidation.
Figure 7. The hourly concentrations of NO$_3^-$, NH$_4^+$, SO$_4^{2-}$, BC, OC, and O$_3$ averaged over the model-captured O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD in BTH in the months of April to October of 2013-2020.

3.3.3 Vertical distributions of O$_3$ and PM$_{2.5}$ in O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD

The simulated vertical distributions of O$_3$ and PM$_{2.5}$ averaged over the 18 grids of BTH and the O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD in warm seasons of 2013–2020 are shown in Fig. 8. The vertical distribution of O$_3$ in O$_3$SPD was similar to that in O$_3$&PM$_{2.5}$PD (Fig. 8a). In these two cases, concentrations of O$_3$ increased from the surface to about 975 hPa, remained high between 975 and 819 hPa, and decreased with altitude between 819 and 663 hPa. Although the magnitudes of O$_3$ were close at the surface (61.9 ppbv in O$_3$&PM$_{2.5}$PD and 58.1 ppbv in O$_3$SPD), the concentration of O$_3$
averaged over 975 and 819 hPa was 10.4% higher in O$_3$&PM$_{2.5}$PD than in O$_3$SPD, which was a very unique feature of O$_3$&PM$_{2.5}$PD. For the case of PM$_{2.5}$SPD, the concentrations of O$_3$ were the lowest among the three cases and increased gently with altitude above 975 hPa.

Figure 8b shows the vertical distributions of PM$_{2.5}$ components. In all the cases, PM$_{2.5}$ concentrations were the highest at the surface, and decreased with altitude from the surface to 975 hPa. However, concentrations of PM$_{2.5}$ were quite stable between 975 and 819 hPa for O$_3$SPD (about 36.4 µg m$^{-3}$) and O$_3$&PM$_{2.5}$PD (about 58.1 µg m$^{-3}$), corresponding to the stable O$_3$ levels at these altitudes in these two cases (Fig. 8a). For PM$_{2.5}$SPD, while PM$_{2.5}$ concentration at the surface was the highest among the three cases, it decreased rapidly between 975 and 819 hPa. The averaged PM$_{2.5}$ concentration between 975 and 819 hPa was 52.4 µg m$^{-3}$ in PM$_{2.5}$SPD, which was lower than that in O$_3$&PM$_{2.5}$PD.

**Figure 8.** The vertical distributions of (a) concentrations of O$_3$ (ppb) and (b) PM$_{2.5}$ components (µg m$^{-3}$) of NO$_3^-$, NH$_4^+$, SO$_4^{2-}$, BC, OC averaged over the model-captured O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD in BTH in the months of April to October of 2013-2020.

To further investigate the differences in vertical profiles of NO$_3^-$, NH$_4^+$, SO$_4^{2-}$, BC,
OC, and PM$_{2.5}$ in O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD, the ratios of concentration at 975 hPa to that at the surface as well as the concentration at 819 hPa to that at 975 hPa are shown in Table 1. The concentration of PM$_{2.5}$ decreased largely, with the ratio of PM$_{2.5}$(975 hPa) / PM$_{2.5}$(1005 hPa) of 0.78 in O$_3$&PM$_{2.5}$PD and of 0.74 in PM$_{2.5}$SPD. For each of the PM$_{2.5}$ components, the ratios near the surface (from 1005 to 975 hPa, gray shaded area in Fig. 8) were close in the three types of pollution. While the ratios of NO$_3^-$, NH$_4^+$, BC, OC were in the range of 0.65-0.80, the ratios of SO$_4^{2-}$ were about 0.93-0.98, indicating that SO$_4^{2-}$ concentrations were quite uniform from the surface to 975 hPa in all three types of pollution.

Table 1. The ratios at 975 and 1005 hPa (gray shaded area in Fig. 8) and at 819 and 975 hPa (red frame in Fig. 8) of NO$_3^-$, NH$_4^+$, SO$_4^{2-}$, BC, OC, and PM$_{2.5}$ in O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD in BTH region.

<table>
<thead>
<tr>
<th></th>
<th>NO$_3^-$</th>
<th>NH$_4^+$</th>
<th>SO$_4^{2-}$</th>
<th>BC</th>
<th>OC</th>
<th>PM$_{2.5}$</th>
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</thead>
<tbody>
<tr>
<td>Conc$_{819 , \text{hPa}}$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>O$_3$SPD</td>
<td>0.95</td>
<td>0.90</td>
<td>0.85</td>
<td>0.73</td>
<td>0.73</td>
<td>0.86</td>
</tr>
<tr>
<td>PM$_{2.5}$SPD</td>
<td>0.64</td>
<td>0.68</td>
<td>0.81</td>
<td>0.64</td>
<td>0.63</td>
<td>0.67</td>
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<tr>
<td>Conc$_{975 , \text{hPa}}$</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>O$<em>3$&amp;PM$</em>{2.5}$PD</td>
<td>0.94</td>
<td>0.91</td>
<td>0.87</td>
<td>0.79</td>
<td>0.77</td>
<td>0.89</td>
</tr>
<tr>
<td>O$_3$SPD</td>
<td>0.65</td>
<td>0.77</td>
<td>0.96</td>
<td>0.69</td>
<td>0.70</td>
<td>0.74</td>
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<tr>
<td>Conc$_{975 , \text{hPa}}$</td>
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<td></td>
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<td></td>
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<tr>
<td>PM$_{2.5}$SPD</td>
<td>0.72</td>
<td>0.76</td>
<td>0.93</td>
<td>0.67</td>
<td>0.65</td>
<td>0.73</td>
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<tr>
<td>Conc$_{1005 , \text{hPa}}$</td>
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<tr>
<td>O$<em>3$&amp;PM$</em>{2.5}$PD</td>
<td>0.72</td>
<td>0.80</td>
<td>0.98</td>
<td>0.76</td>
<td>0.73</td>
<td>0.78</td>
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</tbody>
</table>

In the upper layers (975-819 hPa, red rectangle in Fig. 8), the changes in concentrations of pollutants with altitude in PM$_{2.5}$SPD were quite different from those in O$_3$&PM$_{2.5}$PD and O$_3$SPD. The decline of PM$_{2.5}$ from 975 to 819 hPa was slow in O$_3$&PM$_{2.5}$PD (PM$_{2.5}$(819 hPa) / PM$_{2.5}$(975 hPa)=0.89) and O$_3$SPD (0.86) and fast in PM$_{2.5}$SPD.
Considering that the variation of BC with altitude was mainly driven by meteorology (Sun et al., 2020), the vertical variations of other components that differed significantly from BC indicated the influences of chemical processes. In PM$_{2.5}$SPD, NO$_3^-$, NH$_4^+$, OC had about the same ratio as BC (0.64) (with large decreases with height), except for SO$_4^{2-}$ concentration that had a ratio of 0.81. In O$_3$&PM$_{2.5}$PD, the ratios of NO$_3^-$, NH$_4^+$, SO$_4^{2-}$ were 0.94, 0.91, 0.87, respectively, which were much higher than the value of BC (0.79), indicating NO$_3^-$, NH$_4^+$, SO$_4^{2-}$ were quite uniform in the layers of 975-819 hPa with the influence of chemical processes, which will be discussed further in Sect. 3.3.4 below.

### 3.3.4 Process analyses for O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD

The process analysis (PA) is applied to identify the relative importance of atmospheric processes in the three types of pollution. Figure 9 shows the net changes in O$_3$, NO$_3^-$, NH$_4^+$, SO$_4^{2-}$ by the processes of chemical production (Chem), horizontal advection (Horizontal_adv), vertical advection (Vertical_avd), and diffusion (Diff, vertical PBL mixing process) in the GEOS-Chem model, as well as the total of all these processes (i.e., Chem + Diff + Horizontal_adv + Vertical_avd) in O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD.

For O$_3$, the net changes of O$_3$ by all processes were positive at altitudes of 975-819 hPa in O$_3$&PM$_{2.5}$PD and O$_3$SPD, in which Chem had the largest positive contribution (about 1.5 Gg d$^{-1}$), indicating O$_3$ is chemically produced at these layers. For NO$_3^-$ and NH$_4^+$, the nets of all processes increased mass concentrations at 913-819 hPa in O$_3$&PM$_{2.5}$PD and O$_3$SPD, in which Chem and Vertical_avd were positive and Chem had the largest positive contribution. The vertical profiles of Chem were similar for NO$_3^-$ and NH$_4^+$, both of which had the largest positive values at 913-819 hPa (2.83 Gg d$^{-1}$ for NO$_3^-$ and 0.88 Gg d$^{-1}$ for NH$_4^+$), leading to higher concentrations of NO$_3^-$.
and NH$_4^+$ in O$_3$&PM$_{2.5}$PD than in O$_3$SPD and PM$_{2.5}$SPD. For SO$_4^{2-}$, Chem was positive from the surface to 510 hPa with a peak around 819 hPa, resulting in the uniform SO$_4^{2-}$ concentrations at these altitudes as shown in Fig. 8. Chem for SO$_4^{2-}$ was the highest around 819 hPa in O$_3$&PM$_{2.5}$PD, which was related to the strong liquid-phase chemical formation of SO$_4^{2-}$ (Fig. S6). In addition to Chem, Vertical _avd also had positive contributions to the net changes in O$_3$, NO$_3^-$, NH$_4^+$, and SO$_4^{2-}$ at 944-819 hPa. Vertical _avd was negative at 819 hPa and positive between 944 to 819 hPa, implying that the pollutants were transported from 819 hPa to 944 hPa in O$_3$&PM$_{2.5}$PD.

Figure 9. The vertical profiles of net changes in O$_3$, NO$_3^-$, NH$_4^+$, and SO$_4^{2-}$ (Gg d$^-1$) over BTH by each and total of processes. The values were averaged over the model-
captured regional O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD in April-October of 2013-
2020. Overall, NO$_3^-$, NH$_4^+$, and SO$_4^{2-}$ all had larger chemical productions at 913-819 hPa in O$_3$&PM$_{2.5}$PD compared to those in O$_3$SPD and PM$_{2.5}$SPD, accompanied by strong vertical transport from 819 hPa to near the surface, resulting in the quite uniform vertical profiles at 975-819 hPa in O$_3$&PM$_{2.5}$PD. In addition, the vertical profiles of net changes in PM$_{2.5}$ over BTH are shown in Fig. S7 for these three cases. Since NO$_3^-$, NH$_4^+$, and SO$_4^{2-}$ were the major components of PM$_{2.5}$, the PA of PM$_{2.5}$ is similar to that of each component.

3.3.5 Observed AOD in O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD

To try to support the model result that O$_3$&PM$_{2.5}$PD had more uniform vertical profile than PM$_{2.5}$SPD from the surface to 819 hPa altitude, we present the scatter plots of observed AOD (at 440 nm and 675 nm) versus observed PM$_{2.5}$ concentrations in O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD in Fig. 10. AERONET observations of AOD from 2013 to 2020 are available at three sites in BTH (that is, Beijing (39.97°N, 116.38°E), Beijing-CAMS (39.93°N, 116.31°E), Xianghe (39.75°N, 116.96°E)). At Beijing (39.97°N, 116.38°E), AOD (440nm and 675nm) increased with PM$_{2.5}$ concentration in all three types of pollution. However, under the same levels of surface PM$_{2.5}$ concentration, AOD values in O$_3$&PM$_{2.5}$PD were higher than in PM$_{2.5}$SPD, implying that the column burdens of aerosols were generally higher in O$_3$&PM$_{2.5}$PD than in PM$_{2.5}$SPD, which may support the unique vertical distribution of PM$_{2.5}$ in O$_3$&PM$_{2.5}$PD shown in Fig. 8b. The scatter plots at Beijing-CAMS and Xianghe sites are similar and are shown in Fig. S8.
Figure 10. The scatterplots of (a) AOD (440 nm) and (b) AOD (675 nm) versus observed PM$_{2.5}$ concentrations in O$_3$ SPD, PM$_{2.5}$ SPD, and O$_3$&PM$_{2.5}$PD in Beijing (39.97°N, 116.38°E) in April-October of 2013-2020.

3.4 Meteorological conditions for O$_3$ SPD, PM$_{2.5}$ SPD, and O$_3$&PM$_{2.5}$PD over BTH

Figure 11 shows the vertical profiles of RH, T, and OMEGA for O$_3$ SPD, PM$_{2.5}$ SPD, and O$_3$&PM$_{2.5}$PD captured by the model over BTH in the months of April to October from 2013-2020. It should be noted that O$_3$&PM$_{2.5}$PD had an unique vertical distribution of RH. Near the surface, the values of RH in O$_3$&PM$_{2.5}$PD were between those in O$_3$ SPD and PM$_{2.5}$ SPD. However, in the upper layers (883-771 hPa), O$_3$&PM$_{2.5}$PD had the highest RH among the three cases with a peak value of 58.2%.

As a result, the strongest aqueous chemical production of SO$_4^{2-}$ (aqueous oxidation of SO$_2$ by H$_2$O$_2$) occurred in O$_3$&PM$_{2.5}$PD around 819 to 771 hPa (Fig. S6). The vertical profiles of temperature were similar in the three types of pollution, with the lowest temperature in PM$_{2.5}$ SPD. The vertical profiles of OMEGA were different in the three cases. In O$_3$ SPD and O$_3$&PM$_{2.5}$PD, OMEGA had positive values around 819 hPa,
indicating a strong sinking airflow, leading to a downward transport of pollutants. Under O$_3$&PM$_{2.5}$PD, the average values of PBLH and SWGDN were 946.1 m and 257.2 W m$^{-2}$, respectively, which were higher (lower) than those in PM$_{2.5}$SPD (O$_3$SPD) (Fig. S9). Figure 11. The vertical profiles of RH (%), T ($^\circ$C), and OMEGA (Pa s$^{-1}$) averaged over BTH and over the model-captured regional O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD in in April-October of 2013-2020. Figure 12 shows the compositd weather patterns for regional O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD (over 50% cities in the BTH experienced the pollution) that were captured by the model in April-October of 2013-2020. The weather patterns of O$_3$&PM$_{2.5}$PD were similar to some extent to those of O$_3$SPD but were quite different from those of PM$_{2.5}$SPD. In O$_3$&PM$_{2.5}$PD, the BTH region was controlled by westerlies at 500 hPa without cold air intrusion from the north, and was under the high pressure ridge of the Western Pacific Subtropical High (WPSH) at 850 hPa. The strong southerlies at 850 hPa brought moist air from the south (Fig. S10), resulting in a high RH that was beneficial to the aqueous chemical production of SO$_4^{2-}$ in O$_3$&PM$_{2.5}$PD. In O$_3$SPD, BTH was also under the influence of the high pressure ridge of the WPSH at 850 hPa, but it was weaker than in O$_3$&PM$_{2.5}$PD. Besides, the Northeast Cold Vortex (NCV) was located to the southwest of BTH at 850 hPa in O$_3$SPD, leading to dry and warm conditions, which was favorable for the formation of O$_3$. In PM$_{2.5}$SPD, the BTH region was under the influence of both the continental high and the WPSH at 850 hPa.
At the surface, BTH was under the influence of a uniform high pressure with very weak winds and hence stagnate atmosphere, which was conducive to the accumulation of PM$_{2.5}$.

Figure 12. Composites of wind field (m s$^{-1}$) with SLP (sea level pressure) and with geopotential height at 850 hPa and 500 hPa for regional O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD that were captured by the model in April-October of 2013-2020. The solid black rectangle indicates BTH region.

4. Conclusions

We used the observed hourly concentrations of O$_3$ and PM$_{2.5}$ from CNEMC and the model results from the nested-grid version of the GEOS-Chem model to examine
the chemical and physical characteristics of the co-polluted days by O3 and PM2.5 (O3&PM2.5PD) over the BTH region for eight warm seasons (April-October) from 2013 to 2020. The characteristic of O3&PM2.5PD were compared with those of the polluted days by O3 alone (O3SPD) and by PM2.5 alone (PM2.5SPD). In April-October of 2013-2020, the observed O3SPD, PM2.5SPD, and O3&PM2.5PD were 2954, 2148, and 1614 days, respectively, in which 75.0% (2954/3937), 58.1% (2148/3698), and 79.7% (1614/2024) were captured by the GEOS-Chem model, respectively. We carried out compositied analyses of the chemical and physical characteristics for O3SPD, PM2.5SPD, and O3&PM2.5PD by using the samples (days) captured by both the observations and the model.

The chemical characteristics of O3&PM2.5PD were found to be different from those of O3SPD, PM2.5SPD at the surface. O3&PM2.5PD occurred with high levels of atmospheric oxidants (high OH and O3), with higher SOR and NOR compared to those in O3SPD and PM2.5SPD, leading to high concentrations of both O3 and PM2.5. At the surface, the compositied concentrations of NO3-, NH4+, BC, and OC were the highest in PM2.5SPD, while the compositied concentration of SO42- was the highest in O3&PM2.5PD. There was a strong formation of SO42- during the daytime in O3&PM2.5PD in the oxidative atmosphere.

We also found unique features of the vertical distributions of O3 and PM2.5 in O3&PM2.5PD. Concentrations of PM2.5 were stable and high between 975 and 819 hPa in O3&PM2.5PD, unlike those in PM2.5SPD that decreased rapidly with the altitude. In O3&PM2.5PD, the vertical profiles of NO3-, NH4+, and SO42- were quite uniform at 975-819 hPa, corresponding to the stable O3 concentrations at these altitudes. The process analysis (PA) showed that NO3-, NH4+, and SO42- all had larger chemical productions at altitudes of 913-819 hPa in O3&PM2.5PD compared to those in O3SPD.
and PM$_2.5$SPD. The chemical production of SO$_4^{2-}$ had large positive values from the surface to about 500 hPa. The Vertical$_{avd}$ also had positive contributions to the net changes in O$_3$, NO$_3^-$, NH$_4^+$, and SO$_4^{2-}$ at 944-819 hPa in O$_3$&PM$_{2.5}$PD. Therefore, the strong chemical productions at 913-819 hPa accompanied by the downward transport resulted in the quite uniform vertical profiles at 975-819 hPa in O$_3$&PM$_{2.5}$PD.

Figure 13 summarizes the chemical and physical characteristics in O$_3$&PM$_{2.5}$PD, O$_3$SPD, and PM$_{2.5}$SPD in the BTH region. In O$_3$&PM$_{2.5}$PD, the strong chemical productions of O$_3$, NO$_3^-$, NH$_4^+$, and SO$_4^{2-}$ occur at high altitudes of 913-819 hPa where RH is high, and the accompanied downward airflow causes the stable concentrations at 944-819 hPa. The composited PBLH in O$_3$&PM$_{2.5}$PD is about 946.1 m, and the strong mixed diffusion underneath the PBLH leads to high concentrations of pollutants at the ground level. In contrast, O$_3$SPD occurs in hot and dry atmosphere with composited PBLH of 1073.5 m. Strong O$_3$ chemical production occurs around 819 hPa, and O$_3$ is then transported to the surface by downward air flow. The atmosphere is stable and stagnant when PM$_{2.5}$SPD occurs, with the lowest PBLH of 681.8 m. High RH (high chemical formation of PM$_{2.5}$) and the accumulation of aerosols lead to the highest surface-layer PM$_{2.5}$ in PM$_{2.5}$SPD.
Figure 13. A schematic diagram of chemical and physical characteristics in O$_3$SPD, PM$_{2.5}$SPD, and O$_3$&PM$_{2.5}$PD in BTH region.
Data availability.

The GEOS-Chem model is available at https://geos-chem.seas.harvard.edu (last access: 5 August 2022). The observed hourly surface concentrations of air pollutants are derived from the China National Environmental Monitoring Center (https://air.cnemc.cn:18007/, CNEMC, 2022). The simulation results are available upon request from the corresponding author (hongliao@nuist.edu.cn).

Author contributions.

HD and HL conceived the study and designed the experiments. HD performed model simulations and analysed the data. KL, XY, YY, JZ, JJ, and BL provided useful comments on the paper. HD and HL prepared the paper, with contributions from all co-authors.

Competing interests.

The authors declare that they have no conflict of interest.

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