Response to Comments of Reviewer #1

Manuscript number: acp-2022-557
Title: 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

General comments:
In this manuscript the chemical and physical characteristics of O_3 (O_3SPD), $PM_{2.5}$ ($PM_{2.5}$SPD) polluted days and O_3 and $PM_{2.5}$ (O_3&$PM_{2.5}$PD) co-polluted days over BTH are investigated by using the 3-D global chemical transport model (GEOS-Chem). This manuscript is clearly written and well organized, and its conclusions are interesting.

Thanks to the referee for the helpful comments and constructive suggestions. We have revised the manuscript carefully and the point-to-point responses are listed below.

Major concerns/questions:

1. The simulated $PM_{2.5}$ components including NO_3^-, NH_4^+, SO_4^{2-}, BC, and OC are compared against observed $PM_{2.5}$ concentrations, and the comparison shows that the simulated $PM_{2.5}$ had a NMB of -26.9%. Even with the adjusted thresholds, percentages of observed polluted days for $PM_{2.5}$SPD shown in Figure c are lower than for O_3SPD and O_3&$PM_{2.5}$PD. Is the underestimation attributable to some missing primary aerosols?

Response:
Thanks for pointing this out. In this work we calculated $PM_{2.5}$ concentration as the sum of the simulated masses of SO_4^{2-}, NO_3^-, NH_4^+, BC, and OC as in previous studies (*Yang et al., 2016; Dang et al., 2019; Xie et al., 2022*). Although primary aerosols such as mineral dust and sea salt are not the dominant aerosol species in China (*Xuan et al., 2000; Ye et al., 2003; Duan et al., 2006; Zhao et al., 2013*), the absence of them in the calculation of $PM_{2.5}$ contributed to the low biases in simulated $PM_{2.5}$SPD. To clarify this, we have added the following sentences in the first paragraph of Section 3.2.1: "It should be noted that mineral dust and sea-salt aerosols were not considered in this study, because they are not the major aerosol components in China and the concentrations are generally low based on previous measurements (*Xuan et al., 2000; Ye et al., 2003; Duan et al., 2006; Zhao et al., 2013*). However, excluding dust and sea salt may lead to low biases in simulated $PM_{2.5}$ concentrations.".

2. In the analysis two oxidation indicators (sulfur oxidation ratio and nitrogen oxidation ratio) are used, but not assessed. As observed SO_2 and NO_2 concentrations are available at CNEMC, model performance for SO_2 and NO_2 is suggested to be evaluated.

Response:
Following the Reviewer's suggestion, we have added Figure S2 in the Supplementary Material to evaluate the model performance for SO_2 and NO_2. We have also added the following sentences in the second paragraph of Section 3.2.1 to describe the model

performance: "Due to the lack of the publicly accessible long-term observations of $PM_{2.5}$ components in China, we compared the simulated SO_2 and NO_2 (precursors for SO_4^{2-} and NO_3^-) with observations from CNEMC in Fig. S2. The simulated daily mean concentrations of NO_2 (SO_2) agree well with the observations from CNEMC with R of 0.82 (0.78) and MB of -14.9% (9.3%)."

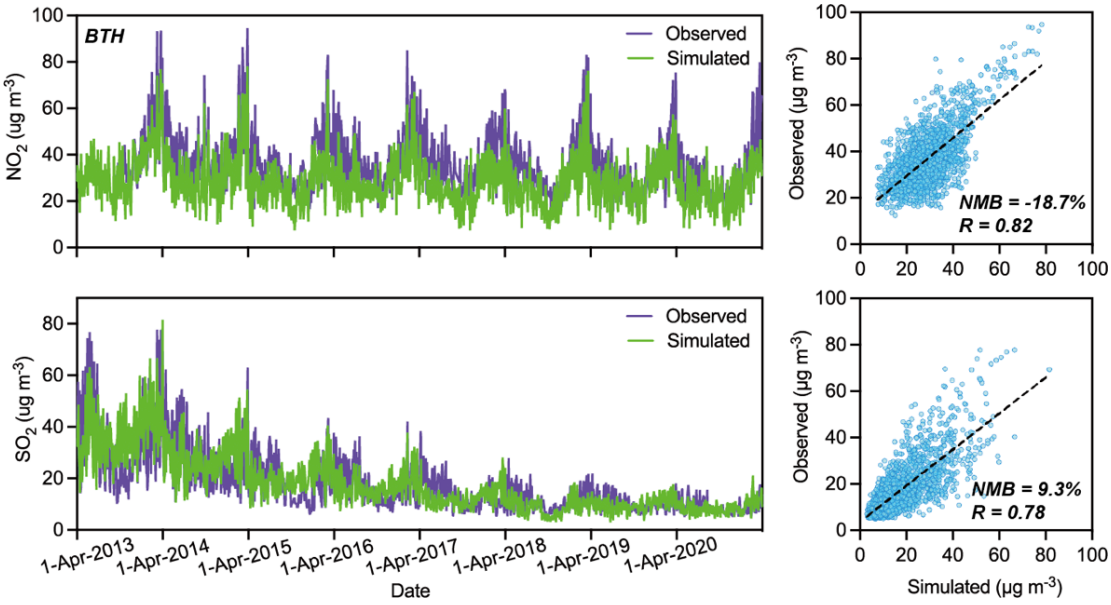

Figure S2. Simulated and observed daily mean surface-layer concentrations of NO_2 and SO_2 as well as the scatterplots of simulated versus observed values for April to October of 2013–2020 in BTH.

3. Figure S5a shows the hourly variations of PBLH (m) averaged in all model-captured O_3SPD (blue), $PM_{2.5}$SPD (yellow), and O_3&$PM_{2.5}$PD (purple). Average PBLH at noon time for O_3SPD and O_3&$PM_{2.5}$PD is over 2000m, why are they so high? Figure S5b shows the daily anomaly of PBLH for O_3SPD and O_3&$PM_{2.5}$PD at night time exceeds -500m, while at noon time over 1000m. How does PBLH usually change over BTH?

Response:

The hourly variations of PBLH were taken from MERRA-2. Hourly PBLH values averaged over all days in the warm months (April-October) of 2013-2020 in BTH are shown in Figure R1. PBLH reached the highest value of 1842 m at 14:00 and the lowest value of 300 m at 6:00. The hourly variation of PBLH over BTH from MERRA-2 agrees closely with observations. *Guo et al. (2016)* used the fine-resolution sounding observations of 391552 profiles from January 2011 to July 2015 across China and reported that PBLH in BTH averaged over summers was around 1600-2000 m at 14:00 and 100-350 m at 2:00. *Tang et al. (2021)* carried out two field campaigns in Shijiazhuang, the area with serious air pollution in BTH, from August 25 to September 19, 2018 (late summer) and from June 8 to July 2, 2019 (early summer). They found that the highest PBLH during the daytime in summer was around 1800 m in O_3 polluted days.

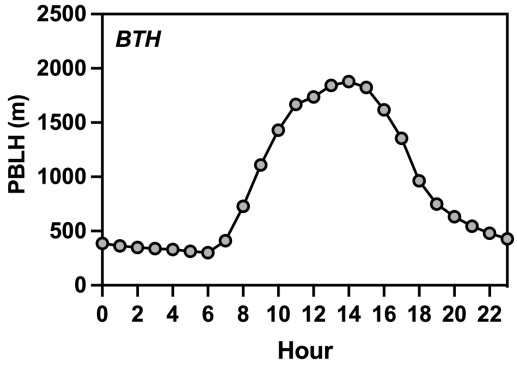

Figure R1. Hourly variation of PBLH from MERRA2 averaged over all days in the warm months (April-October) of 2013-2020 in BTH.

4. Figure S6 shows the vertical profile of SO_4^{2-} chemical production. Why is SO_4^{2-} chemical production larger at high levels than at low levels? Is it associated with cloud or high relative humidity? How is SO_2 concentration distributed vertically? How to understand the difference between O_3SPD and $PM_{2.5}$SPD?

Response:

The vertical profile of SO_4^{2-} chemical production from aqueous oxidation shown in Figure S6 was associated with cloud and relative humidity (RH) (see Figures R2(a)-R2(c) below). The strongest aqueous chemical production of SO_4^{2-} occurred around 819 to 771 hPa where cloud optical depth (OPTDEPTH) and RH peaked. Clouds and high RH were conductive to the aqueous chemical production of SO_4^{2-}. As a result, SO_4^{2-} chemical production was larger at high levels than at low levels.

Figure R2(d) below shows the vertical distributions of SO_2 in the model-captured O_3SPD, $PM_{2.5}$SPD, and O_3&$PM_{2.5}$PD. For all the cases, SO_2 concentrations were the highest at the surface, decreased rapidly with height from the surface to 975 hPa, and then declined slowly at 944-819 hPa.

The differences between O_3SPD and $PM_{2.5}$SPD in Figure S6 indicated in the differences in vertical distribution of the chemical production of SO_4^{2-}, which have been explained in the first paragraph of this response.

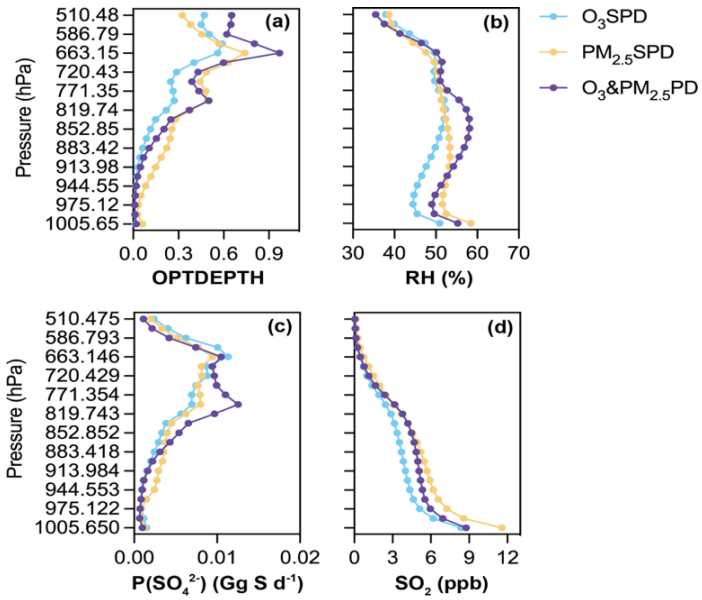

Figure R2. The vertical distributions of (a) cloud optical thickness (OPTDEPTH), (b) relative humidity (RH), (c) SO_4^{2-} chemical production from aqueous oxidation ($P(SO_4^{2-})$), and (d) SO_2 averaged over the model-captured O_3SPD, $PM_{2.5}$SPD, and O_3&$PM_{2.5}$PD in BTH in the months of April to October of 2013-2020.

5. It is interesting to see Figure 8a that O_3 levels for O_3SPD are lower than for O_3&$PM_{2.5}$PD. Does it mean high $PM_{2.5}$ leads to increase in O_3? Figure 8b also shows BC is well mixed vertically up to ~819 hPa. Is it an average for all selected days?

Response:

In this study, we found that high O_3 levels lead to increases in $PM_{2.5}$ in O_3&$PM_{2.5}$PD for the following reasons: (1) O_3&$PM_{2.5}$PD occurred with high levels of atmospheric oxidants (OH and O_x), high SOR and NOR, leading to high concentrations of $PM_{2.5}$, (2) the vertical profiles of NO_3^-, NH_4^+, and SO_4^{2-} were quite uniform at 975-819 hPa, corresponding to the stable O_3 concentrations at these altitudes, as confirmed by the process analysis.

However, high $PM_{2.5}$ concentrations usually lead to reductions in O_3, as reported by previous studies. *Li et al. (2019)* reported that $PM_{2.5}$ influences O_3 chemical production through the uptake of both HO_x and NO_x radicals, which suppressed O_3 production under high $PM_{2.5}$ ($PM_{2.5}$ > 60 μg m^{-3}) in the summer of 2013-2018 in the North China Plain. *Yang et al. (2022)* found that the aerosol-photolysis and aerosol-radiation interactions caused significant decreases in daytime surface-layer O_3 concentrations during multi-pollutant air pollution episodes.

Since the concentrations of BC were small and not easily visible in Figure 8b, we present the vertical distributions of BC in Figure R3 below, which are averaged over all selected samples of the three types of pollution (i.e., 2954 samples of O_3SPD, 2148 samples of $PM_{2.5}$SPD, and 1614 samples of O_3&$PM_{2.5}$PD). The variation of BC with

altitude was mainly driven by meteorology. The ratio of concentration at 819 to that at 975 hPa for BC and other $PM_{2.5}$ components is shown in Table 1 of our manuscript for O_3SPD, $PM_{2.5}$SPD, and O_3&$PM_{2.5}$PD. The $BC_{(819\ hPa)}$ /$BC_{(975\ hPa)}$ was 0.73, 0.64, and 0.79 in O_3SPD, $PM_{2.5}$SPD, and O_3&$PM_{2.5}$PD, respectively. 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. We have discussed these characteristics in Section 3.3.4.

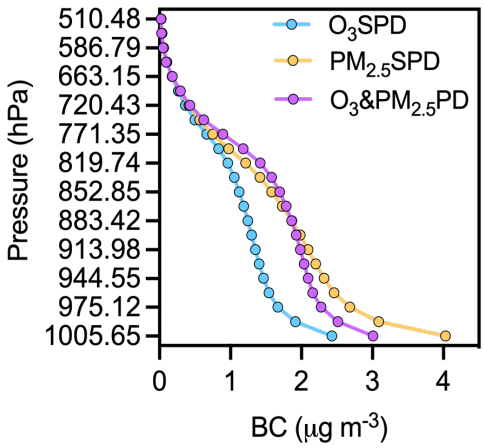

Figure R3. The vertical distributions of BC averaged over the model-captured O_3SPD, $PM_{2.5}$SPD, and O_3&$PM_{2.5}$PD in BTH in the months of April to October of 2013-2020.

Table 1. The ratio of concentration at 819 to that at 975 hPa for NO_3^-, NH_4^+, SO_4^{2-}, BC, OC, and $PM_{2.5}$ averaged over O_3SPD, $PM_{2.5}$SPD, and O_3&$PM_{2.5}$PD in BTH.

		NO_3^-	NH_4^+	SO_4^{2-}	BC	OC	$PM_{2.5}$
$Conc_{819\ hPa}$/ $Conc_{975\ hPa}$	O_3SPD	0.95	0.90	0.85	0.73	0.73	0.86
	$PM_{2.5}$SPD	0.64	0.68	0.81	0.64	0.63	0.67
	O_3&$PM_{2.5}$PD	0.94	0.91	0.87	0.79	0.77	0.89

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