

## Response to Comments of Reviewer #2

**Manuscript number:** acp-2022-557

**Title:** Composited analyses of the chemical and physical characteristics of co-polluted days by ozone and PM<sub>2.5</sub> over 2013–2020 in the Beijing–Tianjin–Hebei region

### General comments:

In recent years, decreases in PM<sub>2.5</sub> but increases in O<sub>3</sub> over eastern China make the co-occurrences of PM<sub>2.5</sub> and O<sub>3</sub> polluted days (O<sub>3</sub>&PM<sub>2.5</sub>PD) an important issue related to human health. In this work, Dai et al. explored the chemical and synoptic characteristics of O<sub>3</sub>&PM<sub>2.5</sub>PD in Beijing-Tianjin-Hebei (BTH) region within a GEOS-Chem framework. They provided comprehensive analysis and concrete details in the differences among PM<sub>2.5</sub> alone polluted days (PM<sub>2.5</sub>SPD), O<sub>3</sub> alone polluted days (O<sub>3</sub>SPD) and O<sub>3</sub>&PM<sub>2.5</sub>PD. Results are novel and of scientific significance. I would like to suggest publication after addressing my comments below:

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:

1. I suggest authors to separate Section 3.3 into two or three parts, where the chemical characteristics, vertical profile and process analysis are described respectively. The current demonstration looks not very logistic and thus makes it hard to follow.

#### Response:

This paper is focused on the characteristics of chemical composition in O<sub>3</sub>SPD, PM<sub>2.5</sub>SPD, and O<sub>3</sub>&PM<sub>2.5</sub>PD, thus the description of the chemical characteristics is a little bit long, but logical. To make this section easier to follow, we have added the following sentences in the first paragraph of Section 3.3 to act as a guide to the readers: “In this section, to investigate the chemical characteristics of O<sub>3</sub>SPD, PM<sub>2.5</sub>SPD and O<sub>3</sub>&PM<sub>2.5</sub>PD, we present first the simulated atmospheric oxidants in 3.3.1, and then show the simulated surface concentrations and vertical profiles of PM<sub>2.5</sub> and MDA8 O<sub>3</sub> in 3.3.2 and 3.3.3, respectively, followed by the process analysis in 3.3.4. The observed AOD values to verify the model results are presented in 3.3.5.”.

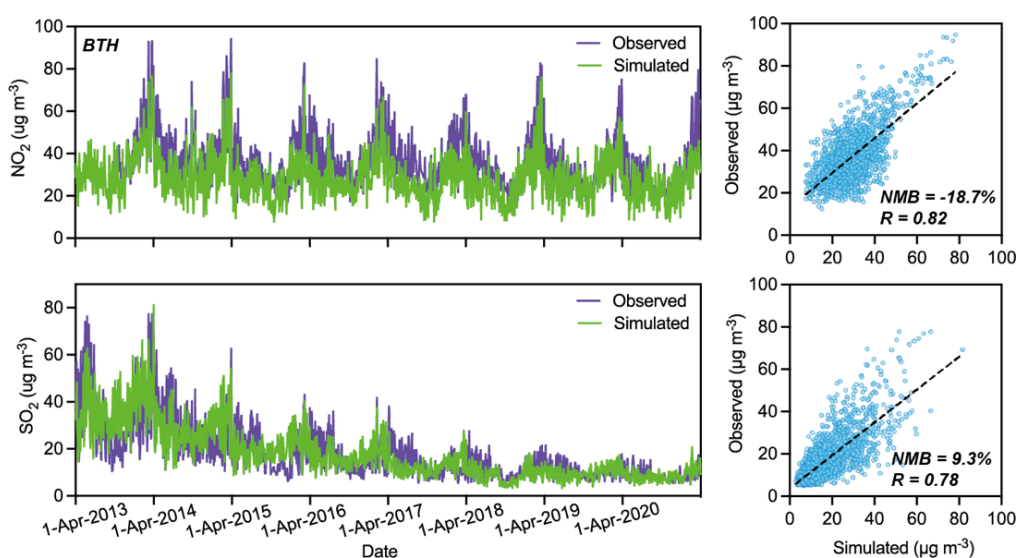
2. Section 3.2, GEOS-Chem still significantly underestimates peak PM<sub>2.5</sub> concentrations as shown in Fig. 3d. Which PM<sub>2.5</sub> components dominate such underestimates? I’m worried that GEOS-Chem incapacity in simulating peak PM<sub>2.5</sub> could significantly influence the following analysis related to the differences in SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> among O<sub>3</sub>SPD, PM<sub>2.5</sub>SPD and O<sub>3</sub>&PM<sub>2.5</sub>PD. At least more evaluation and discussions are necessary.

#### Response:

The Reviewer #1 pointed out that the underestimation of PM<sub>2.5</sub> might be due to the absence of mineral dust and sea salt aerosols in simulated PM<sub>2.5</sub>, therefore 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<sub>2.5</sub> concentrations.”.

Due to the lack of the publicly accessible long-term observations of PM<sub>2.5</sub> components in China, we compared the simulated SO<sub>2</sub> and NO<sub>2</sub> (precursors for SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub>) with observations from CNEMC. The evaluation of model performance for SO<sub>2</sub> and NO<sub>2</sub> in BTH over the eight warm seasons (April to October, 2013–2020) has been added as Figure S2 in the Supplementary Material. 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<sub>2.5</sub> components in China, we compared the simulated SO<sub>2</sub> and NO<sub>2</sub> (precursors for SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub>) with observations from CNEMC in Fig. S2. The simulated daily mean concentrations of NO<sub>2</sub> (SO<sub>2</sub>) 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<sub>2</sub> and SO<sub>2</sub> as well as the scatterplots of simulated versus observed values for April to October of 2013–2020 in BTH.

- Lines 351-354 and Fig. 6, compared to O<sub>3</sub>&PM<sub>2.5</sub>PD, less S was oxidized into SO<sub>4</sub><sup>2-</sup> during PM<sub>2.5</sub>SPD and less N was oxidized into NO<sub>3</sub> during O<sub>3</sub>SPD. Such differences also reflected in the PM<sub>2.5</sub> components in Fig. 6. Are there any explanations about that? In addition, I’m curious what are the dominant oxidation pathways (e.g. SO<sub>2</sub> oxidation through H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, OH or NO<sub>2</sub>) of SO<sub>2</sub> and NO<sub>x</sub> in GEOS-Chem? Can pathways be different among O<sub>3</sub>SPD, PM<sub>2.5</sub>SPD and O<sub>3</sub>&PM<sub>2.5</sub>PD?

**Response:**

In O<sub>3</sub>SPD, PM<sub>2.5</sub>SPD, and O<sub>3</sub>&PM<sub>2.5</sub>PD, 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. Compared to O<sub>3</sub>&PM<sub>2.5</sub>PD, SOR was lower in PM<sub>2.5</sub>SPD, which was due to the lower atmospheric oxidation capacity and hence less SO<sub>4</sub><sup>2-</sup> generation in PM<sub>2.5</sub>SPD. Compared to O<sub>3</sub>&PM<sub>2.5</sub>PD, NOR was lower in O<sub>3</sub>SPD because O<sub>x</sub> (O<sub>x</sub> = O<sub>3</sub> + NO<sub>2</sub>) was lower in O<sub>3</sub>SPD. We have clarified these reasons in the second paragraph of Section 3.3.1.

The formation pathways of SO<sub>4</sub><sup>2-</sup> mainly include the gas-phase oxidation of SO<sub>2</sub> by OH and the in-cloud oxidation of SO<sub>2</sub> by O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. The process that influences NO<sub>3</sub><sup>-</sup> concentration is the gas-to-aerosol conversion of HNO<sub>3</sub> to form NO<sub>3</sub><sup>-</sup> in GEOS-Chem as reported by *Mu et al. (2014)*. As for the dominant pathway for SO<sub>4</sub><sup>2-</sup>, the in-cloud SO<sub>4</sub><sup>2-</sup> formation is known as the major source of global SO<sub>4</sub><sup>2-</sup> because aqueous-phase oxidation of S(IV) by H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> occurs much more rapidly than gas-phase oxidation of SO<sub>2</sub> by OH (*Barth et al., 2000; Ervens, 2015*). Previous modeling studies concluded that a dominant fraction of SO<sub>4</sub><sup>2-</sup> (60–90%) is formed via in-cloud aqueous chemistry globally (*Dovrou et al., 2019; Ervens, 2018; Liao et al., 2013; Harris et al., 2013; Ma and Salzen, 2006*).

The GEOS-Chem's fullchem simulation outputs only the in-cloud SO<sub>4</sub><sup>2-</sup> formation pathway, which is the dominant pathway for SO<sub>4</sub><sup>2-</sup> as mentioned in the above paragraph. We don't think the pathways were different among O<sub>3</sub>SPD, PM<sub>2.5</sub>SPD and O<sub>3</sub>&PM<sub>2.5</sub>PD, but the values of process analyses for chemistry were different because of the different chemical and physical conditions.

4. In Fig.9, I'm confused about the totally different diffusion profile in SO<sub>4</sub><sup>2-</sup> relative to NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>. In the PBL, air pollutants are supposed to diffuse following concentration gradients. For NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, strong chemical production happened in upper layers (913-771 hPa), where diffusion contributions at this altitude were negative, meaning the diffusion of new-generated NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> diffused through PBL. It is reasonable. However, SO<sub>4</sub><sup>2-</sup> diffusion were still positive at altitude where chemical production was strong, which seems against the concentration gradients. It might also be related to the constant SO<sub>4</sub><sup>2-</sup> profile in Fig. 8, which is interesting but I could not find clear explanations in this manuscript.

**Response:**

The vertical profile, chemical production, and diffusion of SO<sub>4</sub><sup>2-</sup> were different from those of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>. Because of the diffusion and chemical production of SO<sub>4</sub><sup>2-</sup>, the profile of SO<sub>4</sub><sup>2-</sup> remained uniform and did not decrease with increasing altitude. To clarify that, we have added explanations in the second paragraph of Section 3.3.4: "Chem and Diff of SO<sub>4</sub><sup>2-</sup> were different from those of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>. For SO<sub>4</sub><sup>2-</sup>, Chem was positive from the surface to 510 hPa with a peak around 819 hPa, and Diff was positive at 819-771 hPa but negative from 819 hPa to the surface, which resulted in the uniform SO<sub>4</sub><sup>2-</sup> profile."

5. I suggest authors to summarize some highlights logistically in conclusions, e.g. what are the major differences in chemical mechanisms among O<sub>3</sub>SPD, PM<sub>2.5</sub>SPD and O<sub>3</sub>&PM<sub>2.5</sub>PD? What meteorological factors or synoptic patterns drives the differences? Also, although authors made very comprehensive analysis, one important question remained not very clear to me: Why O<sub>3</sub>&PM<sub>2.5</sub>PD only occurred at part of the O<sub>3</sub>SPD or PM<sub>2.5</sub>SPD? Which one among chemical mechanisms, vertical profile and meteorology drives the differences?

**Response:**

The major differences in chemical mechanisms among O<sub>3</sub>SPD, PM<sub>2.5</sub>SPD and O<sub>3</sub>&PM<sub>2.5</sub>PD were summarized by Figure 13 and described in the last paragraph of the conclusion section. We stated here that “Figure 13 summarizes the chemical and physical characteristics in O<sub>3</sub>&PM<sub>2.5</sub>PD, O<sub>3</sub>SPD, and PM<sub>2.5</sub>SPD in the BTH region. In O<sub>3</sub>&PM<sub>2.5</sub>PD, the strong chemical productions of O<sub>3</sub>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and SO<sub>4</sub><sup>2-</sup> 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<sub>3</sub>&PM<sub>2.5</sub>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<sub>3</sub>SPD occurs in hot and dry atmosphere with composited PBLH of 1073.5 m. Strong O<sub>3</sub> chemical production occurs around 819 hPa, and O<sub>3</sub> is then transported to the surface by downward air flow. The atmosphere is stable and stagnate when PM<sub>2.5</sub>SPD occurs, with the lowest PBLH of 681.8 m. High RH (high chemical formation of PM<sub>2.5</sub>) and the accumulation of aerosols lead to the highest surface-layer PM<sub>2.5</sub> in PM<sub>2.5</sub>SPD.”

As suggested, we have added the following sentences at the end of the last paragraph of the conclusion section to explain the driving factors of O<sub>3</sub>&PM<sub>2.5</sub>PD: “To summarize, O<sub>3</sub>&PM<sub>2.5</sub>PD were characterized by high O<sub>x</sub>, SOR, and NOR, uniform vertical profiles at 975-819 hPa, which were caused by an anomalous high-pressure system at 500 hPa, strong southerlies and high RH at 850 hPa. Meteorological parameters around 850 hPa promoted strong chemical production of secondary aerosols and downward transport, resulting in the unique vertical profiles and high surface concentrations in O<sub>3</sub>&PM<sub>2.5</sub>PD.”

**Specific Comments:**

1. Lines 48-49: Natural sources also have significant contributions to PM<sub>2.5</sub>.

**Response:**

We have revised the sentence: “... and the major PM<sub>2.5</sub> components (nitrate (NO<sub>3</sub><sup>-</sup>), ammonium (NH<sub>4</sub><sup>+</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>), black carbon (BC), organic carbon (OC)) are mainly caused by anthropogenic emissions of aerosols and aerosol precursors.”

2. Line 61: 'observations' should not be capitalized.

**Response:**

Revised.

3. Lines 334-342: I suggest authors to add a table or figure in the main text or supplementary to show the OH evaluation.

**Response:**

We have added Table S1 in the Supplementary Material. The simulated OH concentrations agreed closely with the observed values.

**Table S1.** The comparisons of simulated OH concentrations with observations in BTH.

Site	Time period	Observed OH	Simulated OH	Reference for observation
Beijing (39.6°N, 116.2°E)	Summer 2017	$5.82 \times 10^6$ (averaged)	$2.4 \times 10^6$ (averaged)	Woodward et al. (2020)
Beijing (40°N, 116.3°E)	Winter 2017	$1.5-2.0 \times 10^6$ (daytime)	$1.8-9.2 \times 10^5$ (averaged)	Ma et al. (2019)
Wangdu (38.7°N, 115.2°E)	Summer 2014	$5-15 \times 10^6$ (daytime)	$3.7-9.5 \times 10^6$ (averaged)	Tan et al. (2017)

4. Line 548: From the traditional synoptic definition, WPSH in eastern China should be regions with 500hPa geopotential height larger than 5880 m (or larger than 1520 m at 850hPa). I don't think the high pressure here is WPSH.

**Response:**

We have revised this sentence (see our response to your specific Comment #6).

5. Line 553: Northeast Cold Vortex is not necessary to abbreviate since it no longer appeared in the manuscript.

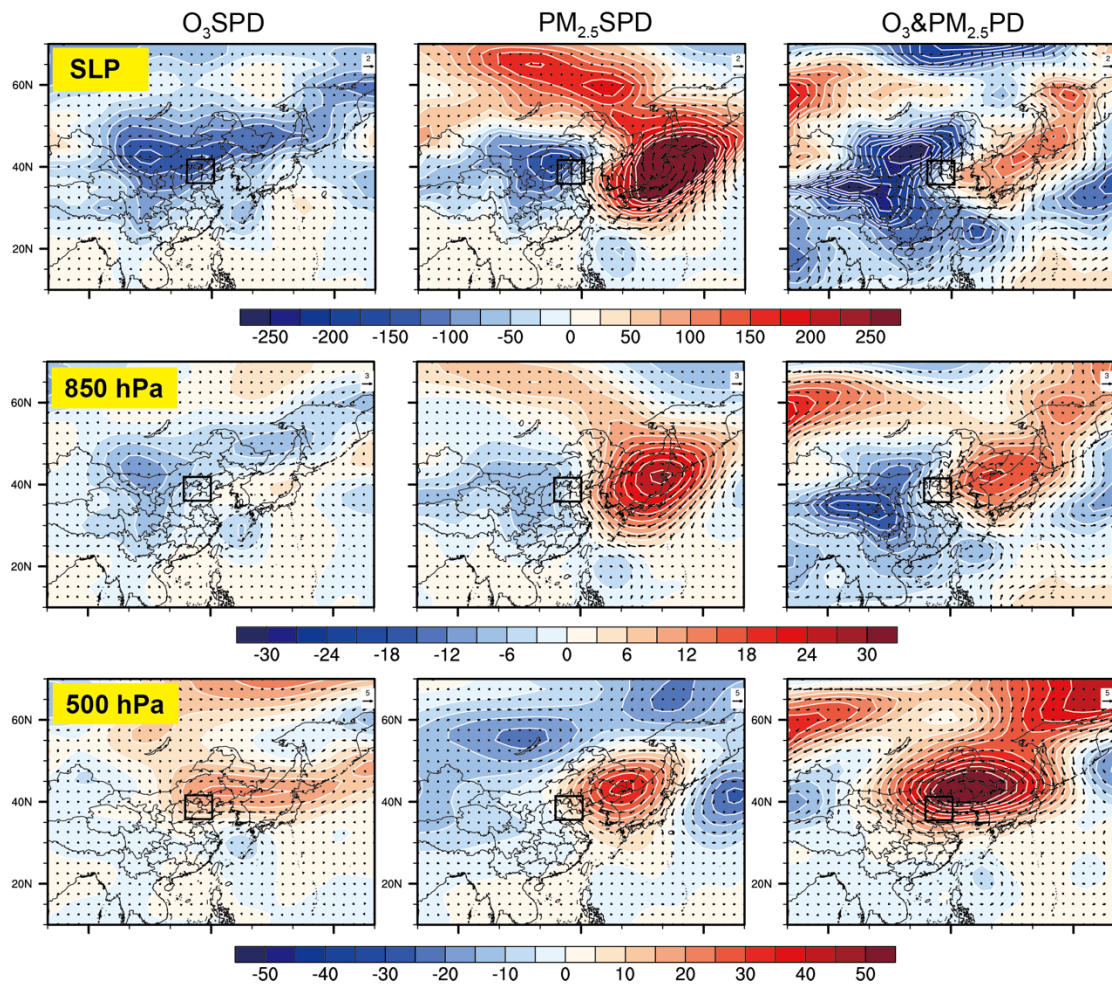
**Response:**

Revised.

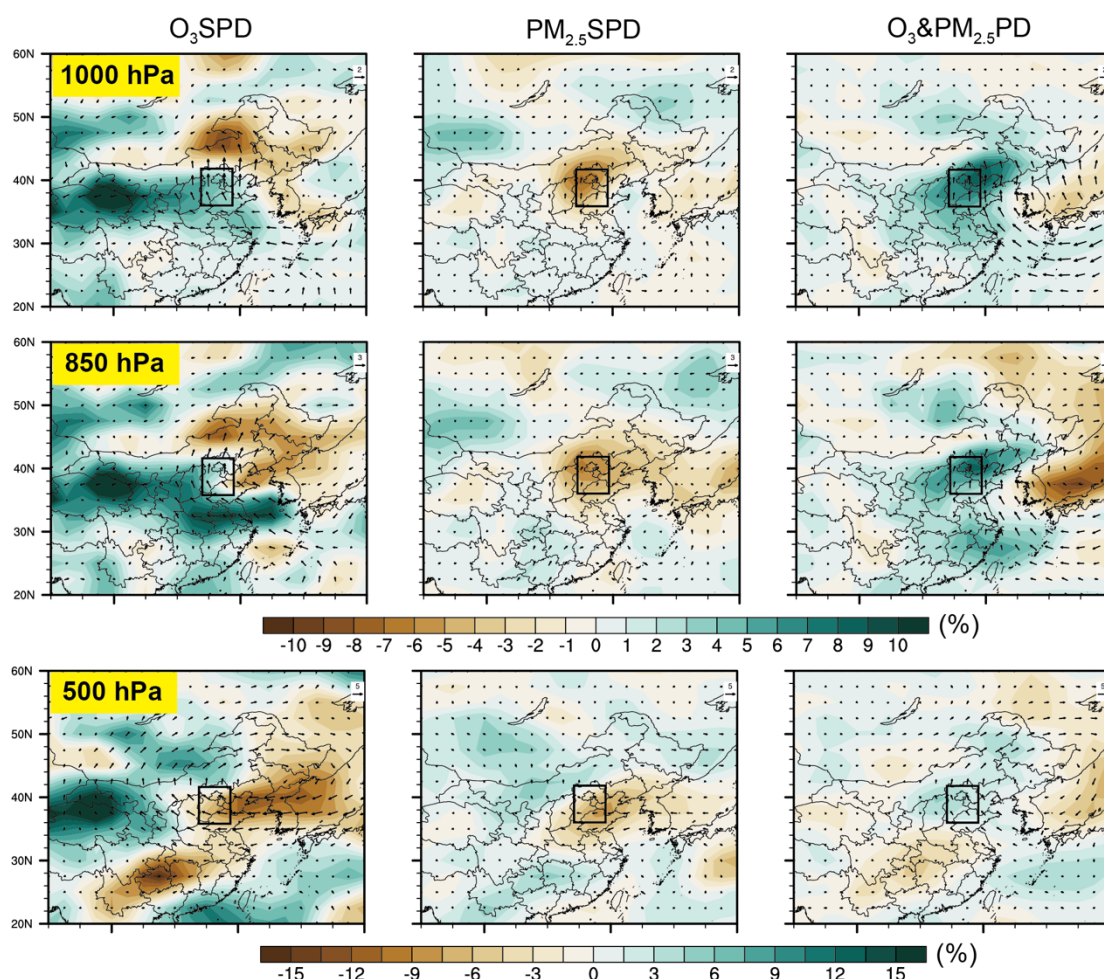
6. Figure 12 and S10: I wonder could the synoptic patterns be clearer if using anomalies rather than absolute values?

**Response:**

Following the Reviewer's suggestion, we have added the anomalous synoptic patterns of Figure 12 and S10 (revised to Figure S12) as Figure S11 and S13, respectively, in the Supplementary Material. We have also added the following sentences in the second paragraph of Section 3.4: "the BTH region was controlled by westerlies and an anomalous high-pressure system at 500 hPa (Figure S11). At 850 hPa, BTH was at the west boundary of an anomalous anticyclone, and the associated strong anomalous southerlies at 850 hPa brought moist air to BTH (Fig. S12 and S13)"



**Figure S11.** Composites of the anomalies of winds (m s<sup>-1</sup>) with SLP (sea level pressure) and with geopotential height at 850 hPa and 500 hPa for regional O<sub>3</sub>SPD, PM<sub>2.5</sub>SPD, and O<sub>3</sub>&PM<sub>2.5</sub>PD that were captured by the model during April-October of 2013-2020. The solid black rectangle indicates the BTH region.



**Figure S13.** Composites of the anomalies of winds ( $\text{m s}^{-1}$ ) with RH (%) at 1000 hPa, 850 hPa, and 500 hPa for regional  $\text{O}_3$ SPD,  $\text{PM}_{2.5}$ SPD, and  $\text{O}_3$ & $\text{PM}_{2.5}$ PD that were captured by the model during April–October of 2013–2020. The solid black rectangle indicates the BT region.

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