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What have we missed when studying the impact of aerosols on surface ozone via changing photolysis rates?

Jinhui Gao et al.

Correspondence to: Ying Li (liy66@sustech.edu.cn)

Table S1: List of geographic source regions in the model domain.

Regions	Details
BJ	Beijing Municipality, China
TJ	Tianjin Municipality, China
HB	Hebei province, China
SD	Shandong province, China
SX	Shanxi province, China
HN	Henan province, China
JS	Jiangsu province, China
AH	Anhui province, China
SH	Shanghai Municipality, China
ZJ	Zhejiang province, China
NECHN	Northeast China, including Heilongjiang, Jilin, and Liaoning provinces, China
NWCHN	Northwest China, including Inner Mongolia, Shaanxi, Ningxia, Gansu, Qingdao, and Xinjiang provinces, China
SWCHN	Southwest China, including Chongqing Municipality, Sichuan, Guizhou, Yunnan and Tibet provinces, China
SCHN	South China, including Hubei, Hunan, Guangxi, Guangdong, Hainan provinces, Hongkong and Macao, China
SECHN	Southeast China, including Jiangxi, Fujiang and Taiwan provinces, China
KOR	Korea, including North Korea and Republic of Korea
SIB	Siberia, including Mongolia and Russia
SEASIA	Southeast Asia, including Thailand, Laos, Philippines, and Vietnam
JPN	Japan
OCEAN	Ocean, including Bohai sea, Huanghai sea, Donghai sea, Nanhai, and parts of western Pacific

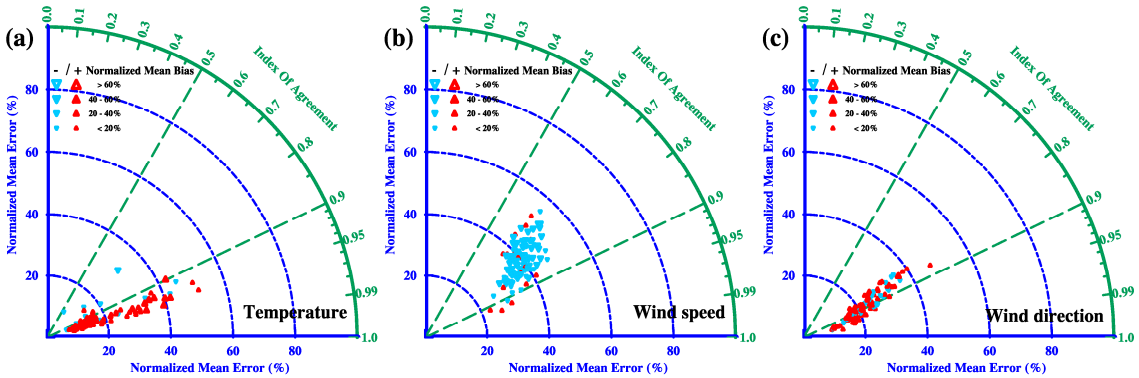


Figure S1: Taylor diagram for displaying model performance metrics on meteorological factors: (a) Temperature at 2m above surface; (b) Wind speed at 10 m above surface; (c) Wind direction at 10 m above surface. The radial distance from origin represents the Normalized Mean Error (NME); the azimuthal position represents the Index of Agreement (IOA); triangles represent the Normalized Mean Bias (NMB), over- and under-estimation are denoted as red up-triangle and blue down –triangle, respectively.

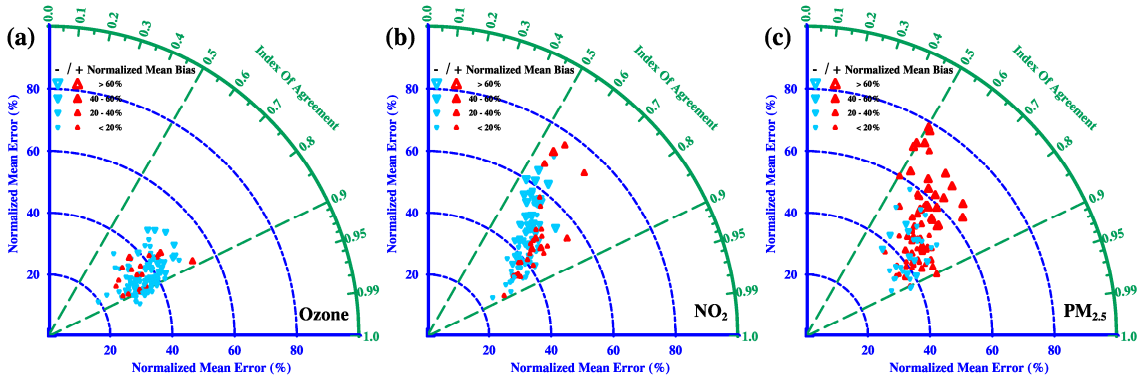


Figure S2: Same to Figure S1 but for air pollutants: (a) ozone; (b) NO_2; (c) $PM_{2.5}$.

Impact of different types of aerosols (light-absorbing and light-scattering) on $J[NO_2]$ profile

Based on the optical properties of aerosols, they can be classified into light-scattering aerosols and light-absorbing aerosols. In addition to talking about the comprehensive effects of aerosols on $J[NO_2]$, it's very necessary to present the effects of light-scattering aerosols and light-absorbing aerosols on $J[NO_2]$, respectively.

Table S2: Refractive indexes of the aerosol species at each wave band in WRF-Chem model

wave band	300nm		400nm		600nm		999nm	
refr. index[a] / species	real[b]	imaginary[c]	real	imaginary	real	imaginary	real	imaginary
SO_4	1.52	1.00×10^{-9}	1.52	1.00×10^{-9}	1.52	1.00×10^{-9}	1.52	1.75×10^{-9}
NO_3	1.50	0.00	1.50	0.00	1.50	0.00	1.50	0.00
NH_4	1.50	0.00	1.50	0.00	1.50	0.00	1.50	0.00
Na	1.51	8.66×10^{-7}	1.50	7.02×10^{-8}	1.50	1.18×10^{-8}	1.47	1.50×10^{-4}
Cl	1.51	8.66×10^{-7}	1.50	7.02×10^{-8}	1.50	1.18×10^{-8}	1.47	1.50×10^{-4}
OC	1.45	0.00	1.45	0.00	1.45	0.00	1.45	0.00
BC	1.85	0.71	1.85	0.71	1.85	0.71	1.85	0.71
OIN	1.55	3.00×10^{-3}	1.55	3.00×10^{-3}	1.55	3.00×10^{-3}	1.55	3.00×10^{-3}

[a] refr. index = refractive index; [b] real = real part; [c] imaginary = imaginary part

In this study, MOSAIC-8bins was used as the aerosol chemistry mechanism. This mechanism includes eight aerosols species: Sulfate (SO_4), Nitrate (NO_3), Ammonium (NH_4), Sodium (Na), Chlorine (Cl), Organic Carbon (OC), Black Carbon (BC), and, Other Inorganics (OIN). According to the source code of WRF-Chem model, the refractive index of each species was listed in Table S2. BC is a typical light-absorbing aerosol. Second to BC, OIN is also treated as light-absorbing aerosol since the imaginary part of which being larger than that of other species. The remaining species are treated as light-scattering aerosols. In order to demonstrating the effects of the two types of aerosols on $J[NO_2]$, two more parallel experiments (Exp3 and Exp4) were designed: Exp3, photolysis rate calculation without considering the optical properties of light-scattering aerosols; Exp4, photolysis rate calculation without considering the optical properties of light-absorbing aerosols. By comparing the results of Exp3 and Exp4 with the results of Exp1 respectively, the effects of light-absorbing aerosols and light-scattering aerosols on $J[NO_2]$ profile can be figured out.

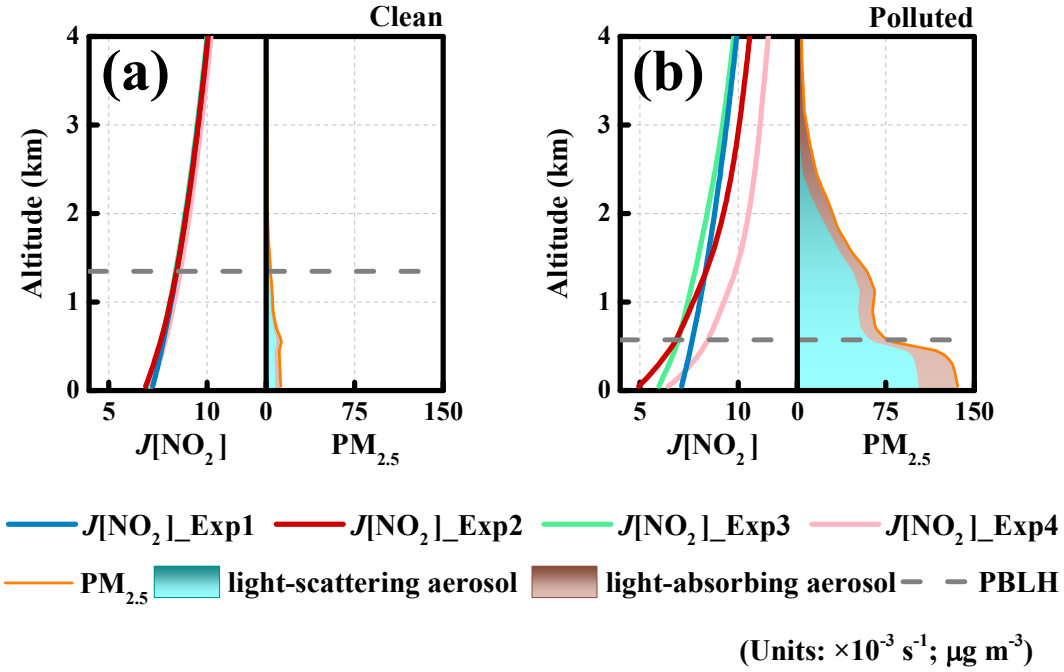


Figure S3: Mean profiles of $J[NO_2]$ and types of aerosols with diameter equal or less than 2.5 μg at 12:00 in clean days (a) and polluted days (b). Mean PBL height of the two kinds of days are also presented in (a) and (b), respectively.

Same as the data collection rule of Fig.3 in the manuscript but for the four experiments, the $J[NO_2]$ profiles under the low-level aerosol condition (clean) and high-level aerosol condition (polluted) at noon (12:00) are presented in Fig. S3. Correspondingly, the profiles of the two types of aerosols (cyan and brown shades) under clean and polluted conditions are also presented in Fig. S3a and S3b, respectively. Under clean condition (Fig. S3a), aerosols were at very low levels and didn't impact $J[NO_2]$ significantly. Consequently, the four profiles didn't show significant differences in vertical direction. Under polluted condition (Fig. S3b), the concentrations of $PM_{2.5}$ were at relatively high levels in the lowest 1.3 km ($PM_{2.5}$ with mean concentration of 90.0 μg m^{-3}; light-absorbing aerosols and light-scattering aerosols are 19.4 μg m^{-3} and 70.6 μg m^{-3}, respectively), especially in the PBL, where the mean concentration of $PM_{2.5}$ reached 123.1 μg m^{-3} (light-absorbing aerosols and light-scattering aerosols are 28.4 μg m^{-3} and 94.7 μg m^{-3}, respectively). Since light-absorbing effect of light-absorbing aerosols, the incident solar irradiance was attenuated and $J[NO_2]$ profile ($J[NO_2]$_Exp3) decreased along with the vertical direction. For light-scattering aerosols, since high concentration being located in lower layer, the incident solar radiation could be scattered backward and enhance the shortwave radiation in higher layer. In this case, $J[NO_2]$ ($J[NO_2]$_Exp4) aloft was enhanced. However, the incident solar irradiance was attenuated at the layers near the surface which leading to the decrease in $J[NO_2]$ near the surface. Combining the effects of the two types of aerosols, the light extinction of aerosols on $J[NO_2]$ ($J[NO_2]$_Exp2) decreased at the lowest 1.3 km but enhanced above 1.3 km.

Unfortunately, since lacking of relevant observations of the aerosol species, concentrations of the simulated aerosols species could not be validated and this may cause some uncertainties to the impacts of different types of aerosols on $J[NO_2]$ profiles. Thus, the results are presented in the supplementary material which is used for qualitatively demonstrating the effects of different types of aerosols on $J[NO_2]$.

Description of the mass balance of chemical species in WRF-Chem

In WRF-Chem model, chemical species undergo the physical and chemical processes that are presented in Fig. S4. The contribution of each process at each time step is represented by the difference between the concentration after the process calculation (C^{new}) and the concentration before the process calculation (C^{old}).

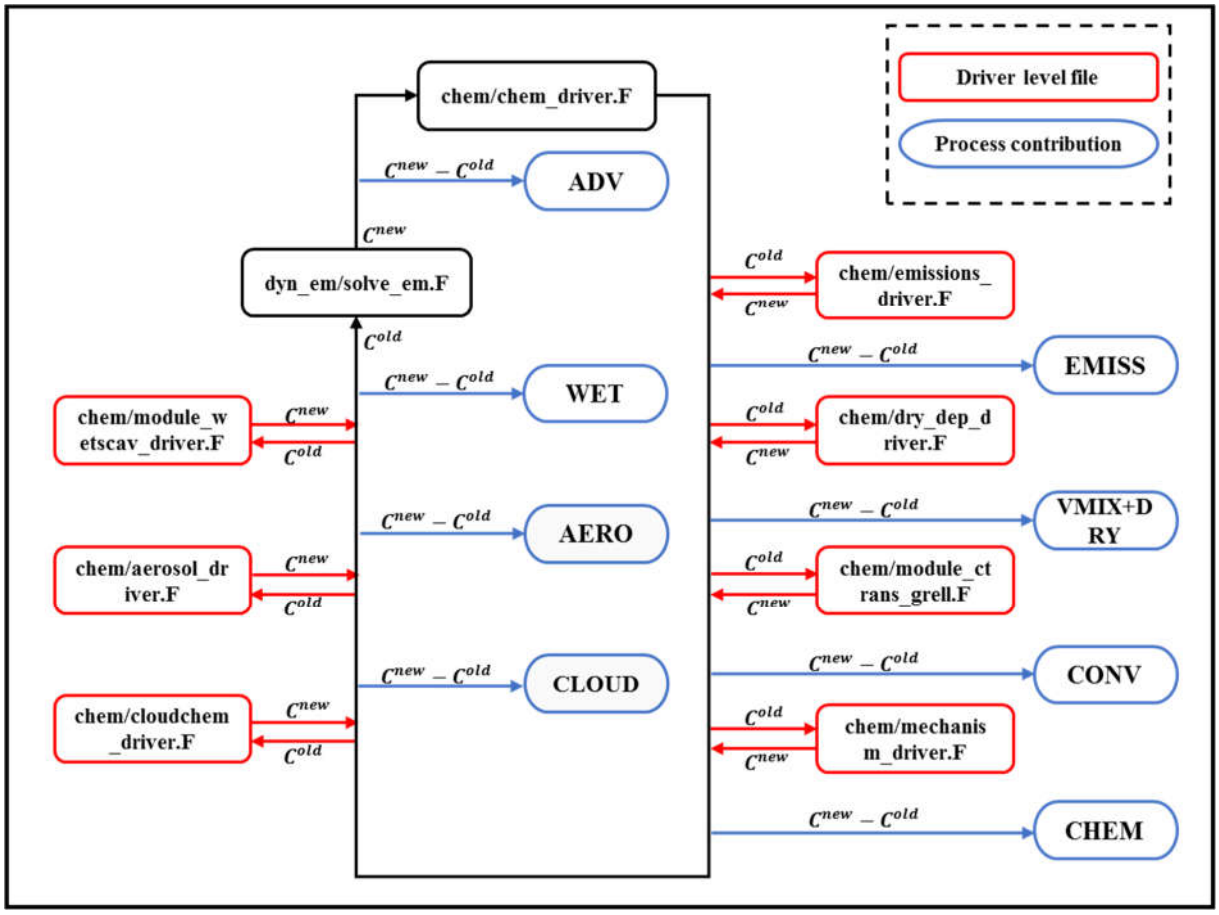


Figure S4: Schematic showing the calculation flow of chemical species in the WRF-Chem model.

In this case, for any chemical species at any grid, the change of concentration (ΔC) at each time step equals to:

$$\Delta C = ADV + EMISS + VMIX + DRY + CONV + CHEM + CLOUD + AERO + WET \quad (1)$$

Among them, ADV is the contribution from advection; EMISS is the contribution from direct emission; VMIX is the contribution from vertical mixing process; DRY is the contribution from dry deposition; CONV is the contribution from

convection; CHEM is the contribution from gas-phase chemistry; CLOUD is the contribution from cloud chemistry; AERO is the contribution from aerosol chemistry; WET is the contribution from wet deposition. For ozone, some of the terms don't contribute the change of ozone (ΔOzone). As a typical secondary pollution, there is no direct emission of ozone in the model and EMISS is 0.0. MOSAIC was used as aerosol chemistry mechanism in this study. This mechanism involves processes such as heterogeneous reactions, gas-particle mass transfer process, nucleation and coagulation. However, ozone doesn't participate in relevant calculations which means AERO is 0.0. Same as aerosol chemistry, ozone also doesn't participate in the calculation of cloud chemistry and the CLOUD is 0.0. Because we selected the simulated data which was under the clear sky conditions, there was no contribution from wet deposition (WET=0.0). In this case, for ΔOzone, the mass balance equation can be simplified to:

$$\Delta Ozone = ADV + VMIX + DRY + CHEM + CONV \quad (2)$$

Since occurring on the ground level, DRY only shows contribution in the first layer in the model domain. Thus, the mass balance equation of ΔOzone at any grid and at each time step can be shown as:

$$\Delta Ozone = \begin{cases} ADV + CHEM + VMIX + CONV + DRY & in\ 1^{st}\ layer \\ ADV + CHEM + VMIX + CONV & above\ 1^{st}\ layer \end{cases} \quad (3)$$

The original WRF-Chem model has provided some processes diagnostic variables (names of these variables are advz_o3, advh_o3, chem_o3, vmix_o3, and conv_o3) to show the contributions of the primary processes to ozone concentrations. According to the original model code, each process diagnostic variable is the accumulation of the difference of the ozone concentration between after and before the corresponding process calculation at each time step. The variables advh_o3 and advz_o3 represent the contributions from horizontal advection and zonal advection. And the contribution of ADV is the sum of advh_o3 and advz_o3 (ADV=advh_o3+advz_o3). The variable chem_o3 represents the contribution of CHEM. Dry deposition occurred at surface which is located in the first layer in the model domain. It is calculated together with vertical mixing process in the subroutine vertmx (chem/module_vertmx_wrf.F) which belongs to the module of dry_dep_driver (chem/dry_dep_driver.F). Thus, in the first layer, the variable vmix_o3 is the sum contribution of VMIX and DRY. And above the first layer, vmix_o3 equals to the contribution of VMIX.

In order to making the discussion of process analysis on surface ozone more clearly, it's necessary to separate the contribution of DRY from vmix_o3. It has been known that, pressure and temperature are not change when doing the dry deposition calculation. Thus, the contribution of DRY to ozone concentration (C_{O3}) at each time step (dt) can be calculated as:

$$DRY = C_{O3} * dvel * dt/dz \quad (4)$$

In which, dvel is the dry deposition velocity of ozone and dz is the height of the grid. And the contribution of VMIX in the first layer at each time step equals to:

$$VMIX = vmix\_o3 - DRY \quad (5)$$

In addition, conv_o3 represented the contribution of CONV which may impact ozone concentration when it occurred in the atmosphere. However, in our study, contribution of CONV was 0.0 during the periods we discussed and was not mentioned in our manuscript.

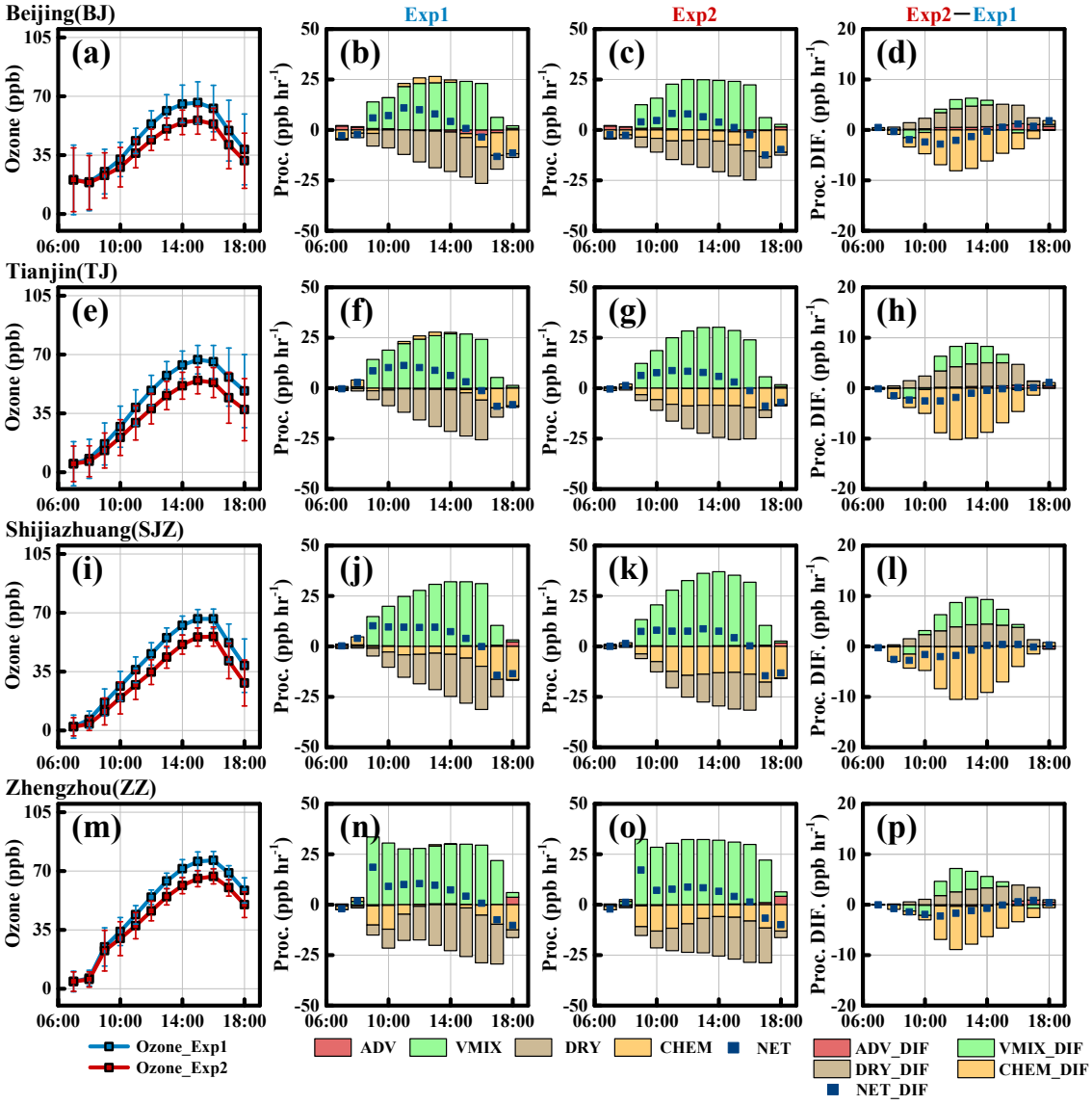


Figure S5: Time series of simulated ozone at surface, corresponding hourly processes and net contributions of ozone in Exp1 and Exp2, the changes of hourly- processes and net contributions induced by aerosol (Exp2-Exp1) over four selected cities from 07:00 to 18:00 LT. (a)~(d) for BJ, (e)~(h) for TJ, (i)~(l) for SJZ, and (m)~(p) for ZZ. For processes, ADV is advection, VMIX is vertical mixing. DRY is dry deposition, CHEM is chemistry, NET is net contribution which is the sum of these mentioned processes contributions. Changes of each contribution induced by aerosol are denoted by ADV_DIF, VMIX_DIF, DRY_DIF, CHEM_DIF, and NET_DIF.

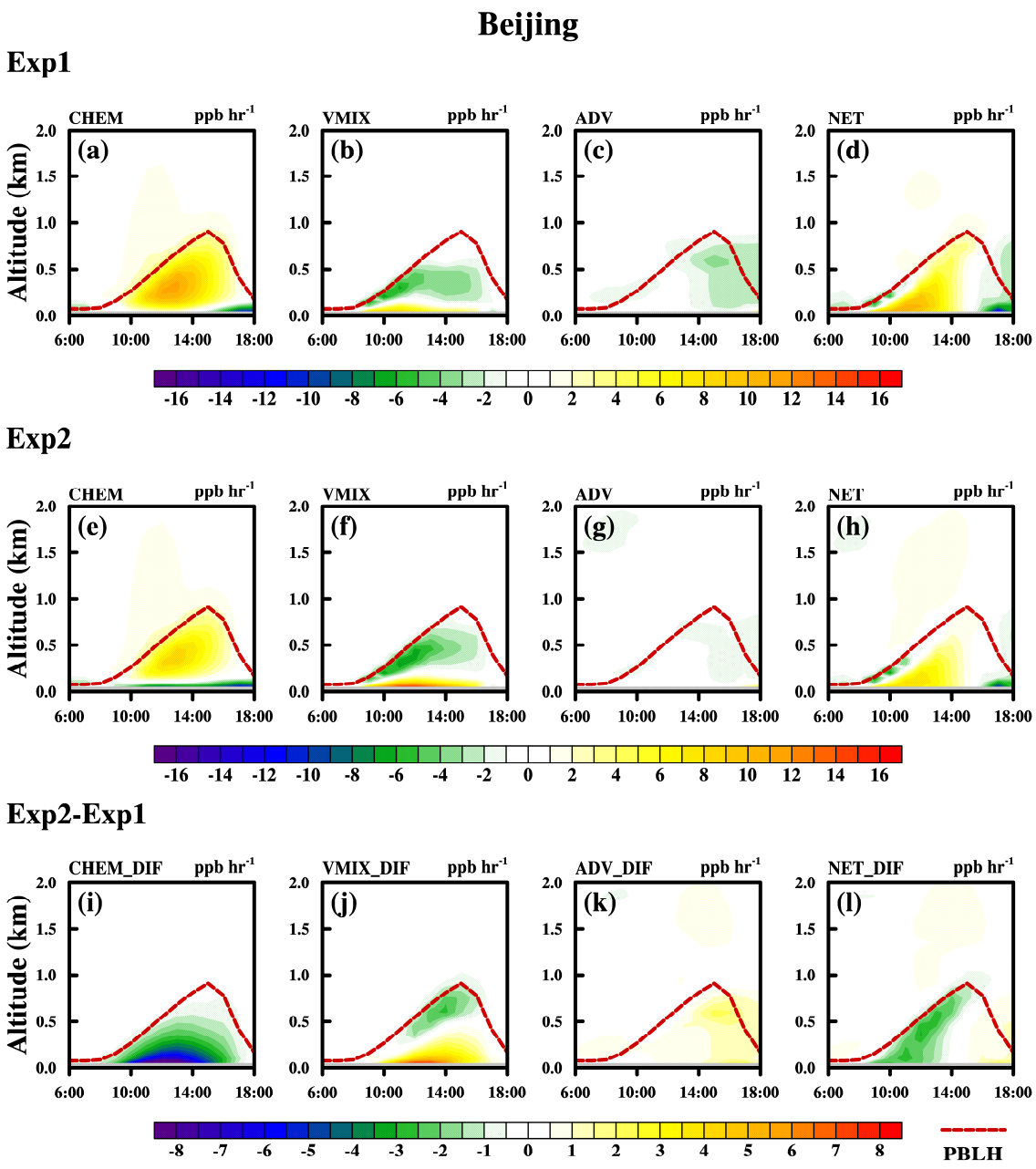
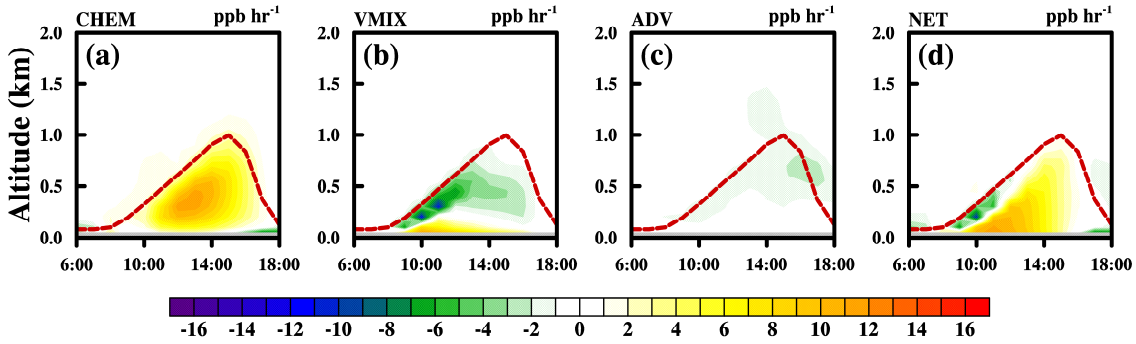


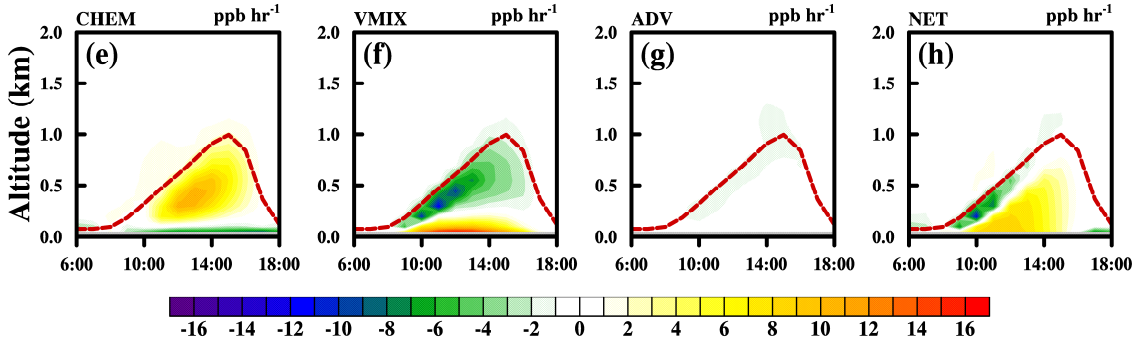
Figure S6: Averaged vertical distributions of processes contributions in function with time in Beijing from 06:00 to 18:00 LT. (a)-(d) for Exp1; (e)-(h) for Exp2; (i)-(l) for the changes of each process contribution due to aerosols (Exp2-Exp1). Red dash lines denote PBLH.

Tianjin

Exp1



Exp2



Exp2-Exp1

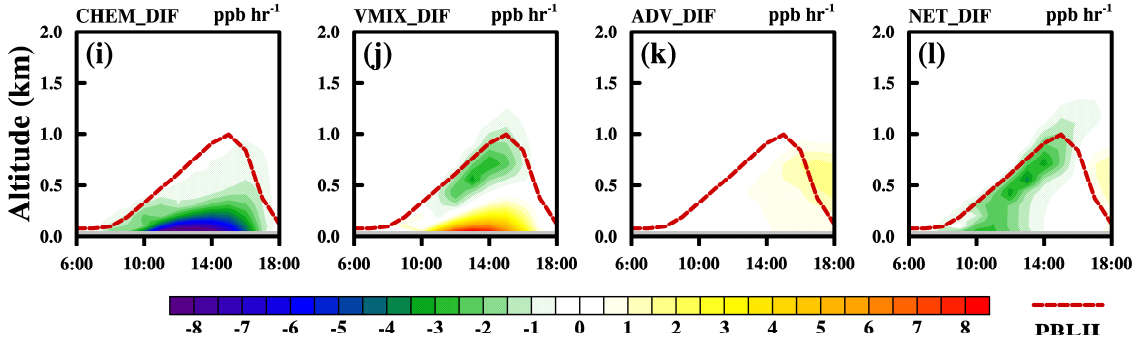
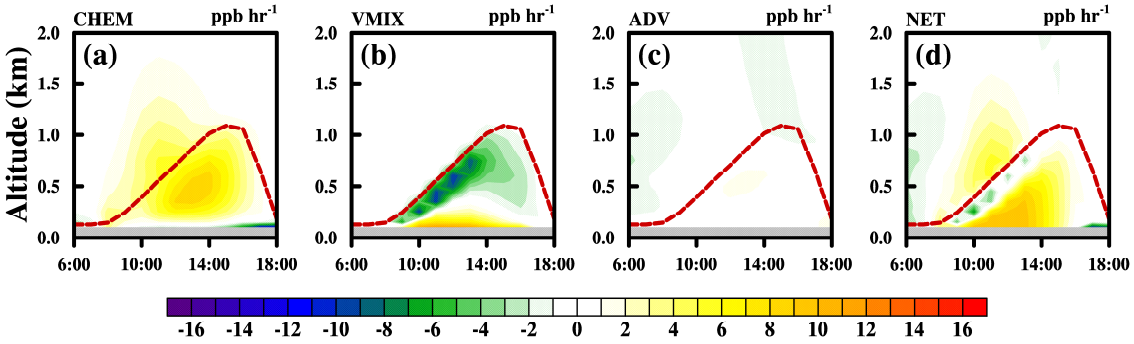


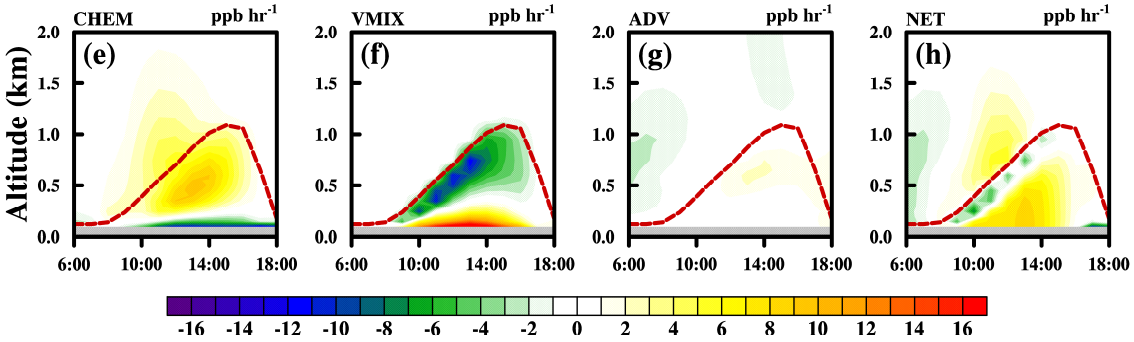
Figure S7: Same to Figure S6 but for Tianjin.

Shijiazhuang

Exp1



Exp2



Exp2-Exp1

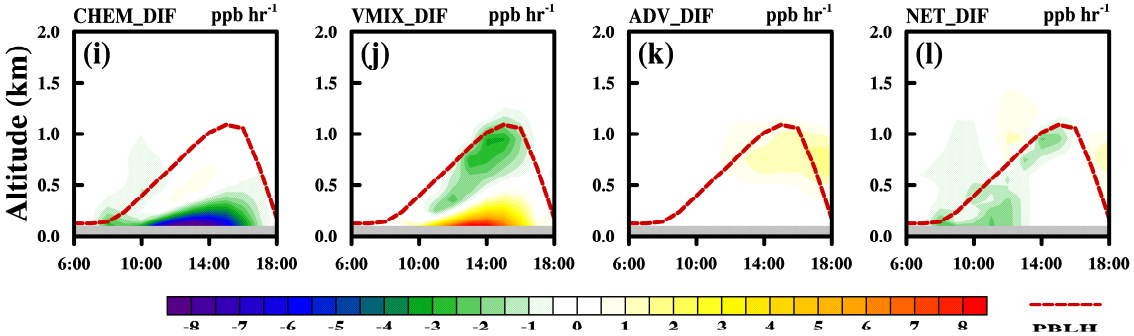


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Figure S8: Same to Figure S6 but for Shijiazhuang.

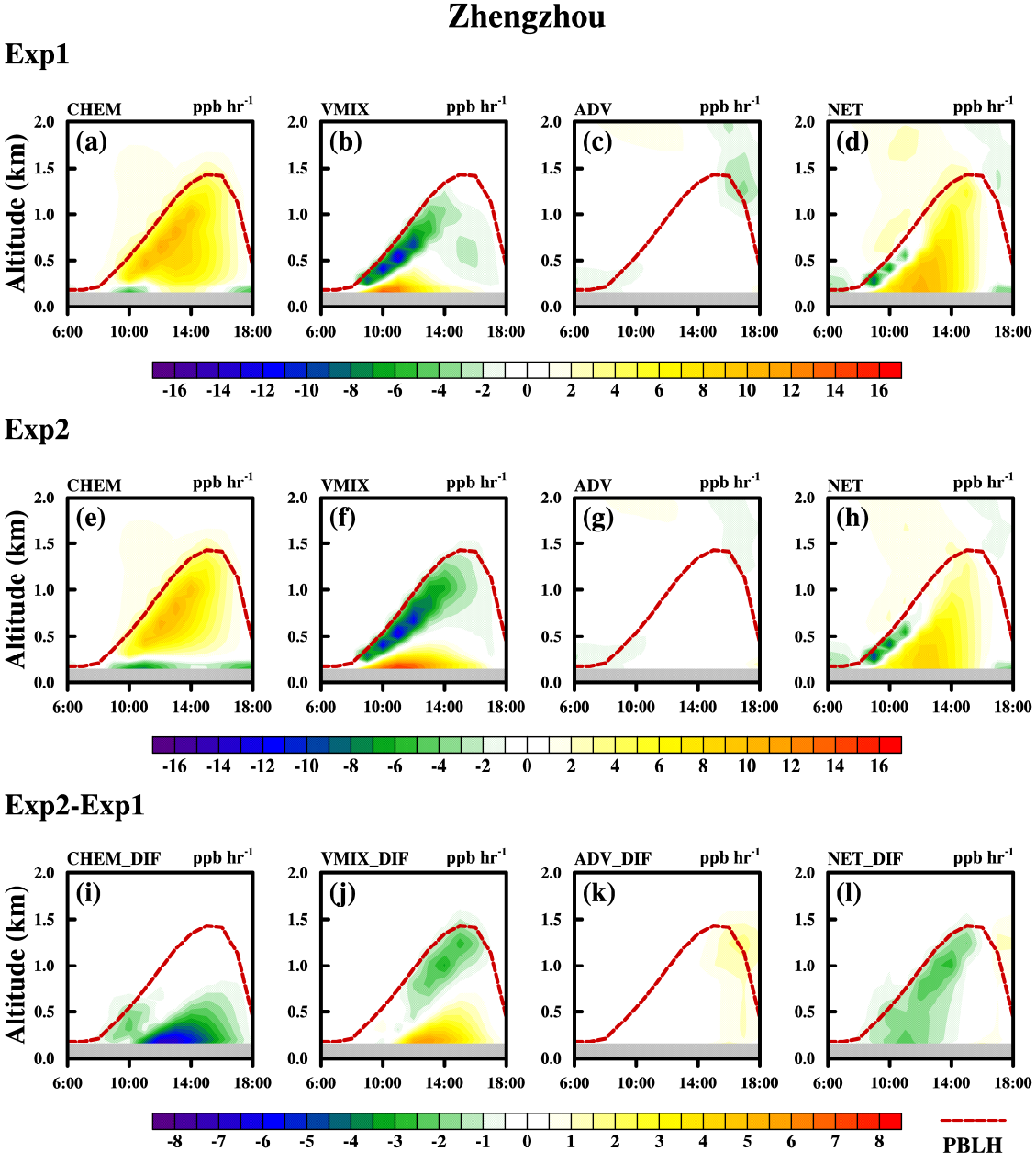

Figure S9: Same to Figure S6 but for Zhengzhou.

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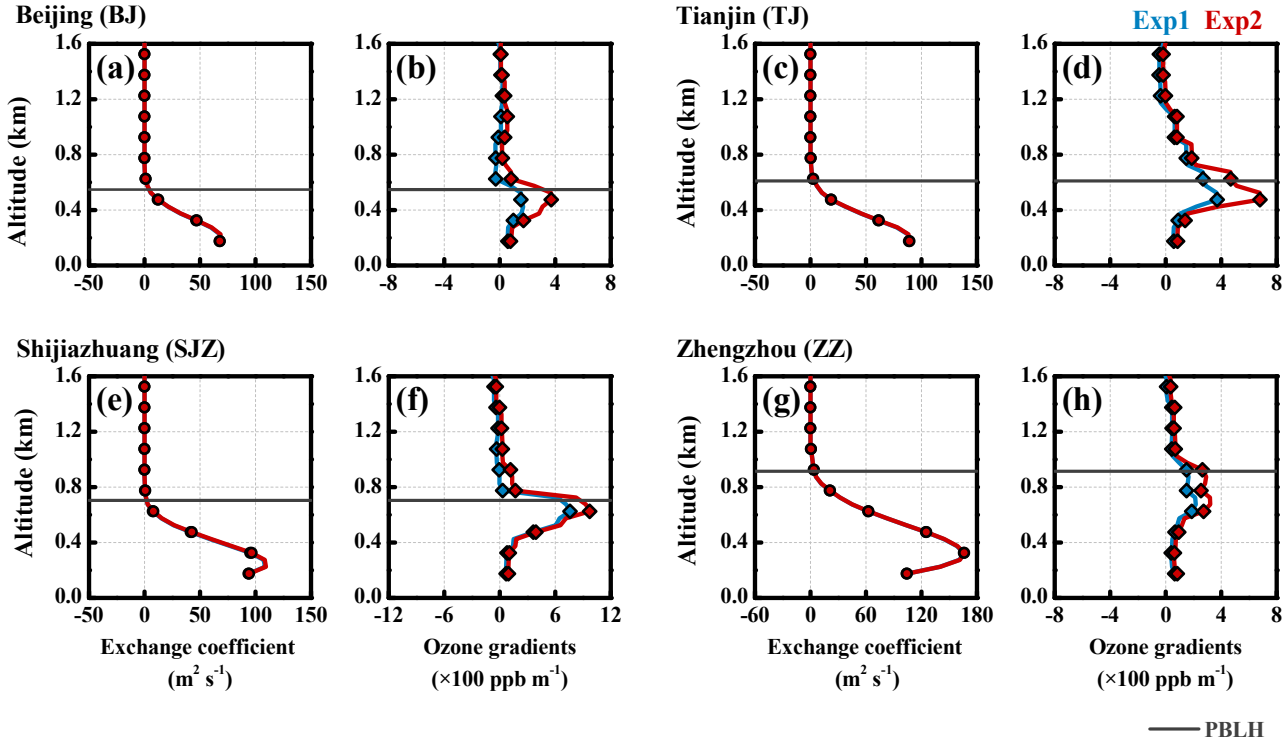

Figure S10: Averaged vertical profiles of turbulence exchange coefficients and vertical gradients of ozone in BJ (a)-(b), TJ (c)-(d), SJZ (e)-(f) and ZZ (g)-(h) of Exp1 and Exp2 at 12:00 AM. Dark gray dash lines denote PBLHs at this time.