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Aerosol–radiation feedback deteriorates the wintertime haze in the North China Plain

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Supplement

The supplement provides description about methodology and model evaluations of air pollutants during the study episode.

Section S1 Methodology

S1.1 Statistical metrics for observation-model comparisons

In the present study, the mean bias (*MB*), root mean square error (*RMSE*) and the index of agreement (*IOA*) are used as indicators to evaluate the performance of WRF-Chem model in simulation against measurements. *IOA* describes the relative difference between the model and observation, ranging from 0 to 1, with 1 indicating perfect agreement.

$$\boldsymbol{MB} = \frac{1}{N}\sum_{i=1}^{N}(\boldsymbol{P_i} - \boldsymbol{O_i})$$

$$\boldsymbol{RMSE} = \left[\frac{1}{N}\sum_{i=1}^{N}(\boldsymbol{P_i} - \boldsymbol{O_i})^2\right]^{\frac{1}{2}}$$

$$\boldsymbol{IOA} = 1 - \frac{\sum_{i=1}^{N}(\boldsymbol{P_i}-\boldsymbol{O_i})^2}{\sum_{i=1}^{N}(|\boldsymbol{P_i}-\overline{\boldsymbol{O}}|+|\boldsymbol{O_i}-\overline{\boldsymbol{O}}|)^2}$$

Where $\boldsymbol{P_i}$ and $\boldsymbol{O_i}$ are the predicted and observed pollutant concentrations, respectively. *N* is the total number of the predictions used for comparisons, and $\overline{\boldsymbol{P}}$ and $\overline{\boldsymbol{O}}$ represents the average of the prediction and observation, respectively.

Section S2 Model Evaluation

Section S2.1 Air pollutants simulations in the NCP

Figure S1 shows the temporal profiles of observed and calculated near-surface $PM_{2.5}$, O_3, NO_2, SO_2 and CO concentrations averaged over monitoring sites in the NCP from 05 December 2015 to 04 January 2016. The model generally tracks well the diurnal variation of near-surface [$PM_{2.5}$] in the NCP, with *IOA* of 0.94, but slightly overestimates [$PM_{2.5}$], with a *MB* of 8.3 μg m^{-3}. The model successfully reproduces the temporal variations of near-surface

O_3 concentrations compared to observations in the NCP, e.g., peak O_3 concentrations in the afternoon due to active photochemistry and low O_3 concentrations during nighttime caused by the NO_x titration, with an *IOA* of 0.94. However, the model generally underestimates the O_3 concentration during nighttime, with a *MB* of -3.6 μg m^{-3}. The model also reasonably well yields the NO_2 diurnal profiles with peaks in the evening, with an *IOA* of 0.86 and a *MB* of 1.6 μg m^{-3}, but sometimes there are considerable overestimations and underestimations. The model generally performs reasonably in predicting the temporal variation of SO_2 concentrations against measurements, with an *IOA* of 0.74. However, considering that SO_2 is mainly emitted from point sources and its simulations are more sensitive to the wind field uncertainties (Bei et al., 2017), the overestimation and underestimation for the SO_2 simulation is rather large, with a *RMSE* of 13.3 μg m^{-3}. Compared with measurements, the temporal profile of the near-surface CO concentration in the NCP is well simulated, with the *IOA* and *MB* of 0.87 and 0.1 μg m^{-3}, respectively.

Section S2.2 Spatial simulations of air pollutants in the NCP

Figure S2 shows the spatial pattern of calculated and observed average near-surface concentrations of $PM_{2.5}$, O_3, NO_2, and SO_2 along with simulated winds from 05 December 2015 to 04 January 2016 in Eastern China. In general, the simulated air pollutants distributions are in good agreement with the measurements, but model biases still exist. The simulated winds are weak or calm during the simulation period, facilitating accumulation of air pollutants and causing the serious air pollution in Eastern China. NCP is the most polluted region due to its massive air pollutants emissions, with the average near-surface [$PM_{2.5}$] generally exceeding 115 μg m^{-3}. The highest average near-surface [$PM_{2.5}$] of more than 150 μg m^{-3} are observed in Beijing, Hebei, Henan, Shandong, and the Guanzhong basin, which are well reproduced by the model. The simulated O_3 concentrations are rather low in the NCP, ranging from 5 to 40 μg m^{-3}, consistent with measurements. The low O_3 concentration during

wintertime haze episodes in the NCP is primarily caused by the weak insolation further attenuated by clouds and aerosols, the titration of high NO_x emissions, and lack of the O_3 transport from outside (Li et al., 2018). Although significant effort has been made to mitigate air pollutants emissions in the NCP, the observed and simulated average NO_2 and SO_2 concentrations are still high, varying from 30 to 100 μg m^{-3} and 20 to 100 μg m^{-3}, respectively. Interestingly, the simulated high SO_2 concentrations are mainly concentrated in cities and their surrounding areas, but the uniform distribution of NO_2 concentrations is predicted in the NCP, showing the substantial contribution of area sources.

Section S2.3 Aerosol species simulations in Beijing

Figure S3 provides the temporal variations of simulated and observed aerosol species at NCNST in Beijing from 05 December 2015 to 04 January 2016. Generally, the WRF-Chem model predicts reasonably the temporal variations of the aerosol species against the measurements. The WRF-Chem model yields the main peaks of the POA concentration compared to observations in Beijing, but frequently underestimates or overestimates the POA concentration, with an *IOA* of 0.80 and a *RMSE* of 17.4 μg m^{-3}. The POA level in Beijing is influenced by local emissions and to a large extent trans-boundary transport from outside during haze days, so its simulation is sensitive to uncertainties from emissions and meteorological fields (Bei et al., 2010, 2012). The model still has difficulties in simulating the SOA concentrations, although the VBS modeling method is used and contributions from glyoxal and methylglyoxal are included in the study, with *IOA* and *MB* of 0.77 and -10.6 μg m^{-3}, respectively. Except the SOA formation and transformation mechanism in the atmosphere, which remains elusive, many factors have potentials to influence the SOA simulation, such as meteorology, measurements, precursors emissions, and SOA treatments (Li et al., 2011a). The model reasonably tracks the temporal variation of the observed sulfate concentration, and the *MB* and *IOA* are 0.6 μg m^{-3} and 0.90, respectively. Aside from SO_2

emissions and simulated meteorological fields, the SO_2 oxidation mechanism in the atmosphere also plays an important role in the sulfate simulation. In addition to direct emissions and SO_2 gas-phase oxidations by hydroxyl radicals (OH) and stabilized criegee intermediates (sCI), the SO_2 oxidation in aerosol water by O_2 catalyzed by Fe^{3+} is considered (Li et al., 2017a). Recent studies have proposed that the aqueous oxidation of SO_2 by NO_2 under the condition of high RH and NH_3 neutralization could interpret the efficient sulfate formation during wintertime haze events (Wang et al., 2016; Cheng et al., 2016). However, the mechanism is still not included in this study, which might further improve the sulfate simulation. The model performs well in simulating the nitrate and ammonium concentrations against observations in Beijing, with *IOAs* of 0.90 and 0.91, respectively.

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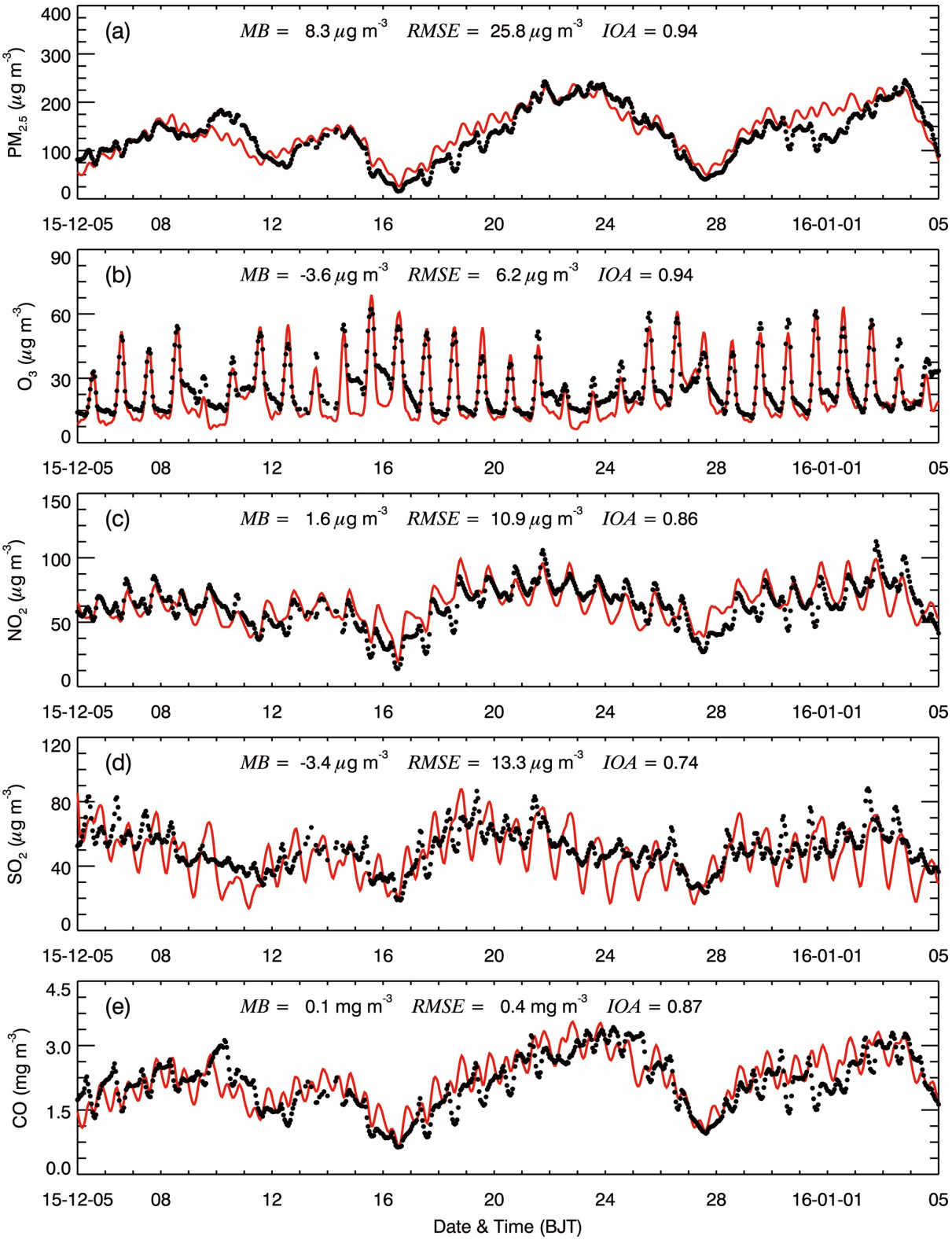
Supplement Figure Captions

Figure S1 Comparison of observed (black dots) and simulated (solid red lines) diurnal profiles of near-surface hourly mass concentrations of (a) $PM_{2.5}$, (b) O_3, (c) NO_2, (d) SO_2, and (d) CO averaged at monitoring sites in the NCP from 05 December 2015 to 04 January 2016.

Figure S2 Pattern comparisons of simulated (color counters) vs. observed (colored circles) near-surface mass concentrations of (a) $PM_{2.5}$, (b) O_3, (c) NO_2, and (d) SO_2 averaged from 05 December 2015 to 04 January 2016. The black arrows indicate simulated surface winds.

Figure S3 Comparison of measured (black dots) and simulated (black line) diurnal profiles of submicron aerosol species of (a) POA, (b) SOA, (c) sulfate, (d) nitrate, and (e) ammonium at NCNST site in Beijing from 05 December 2015 to 04 January 2016.



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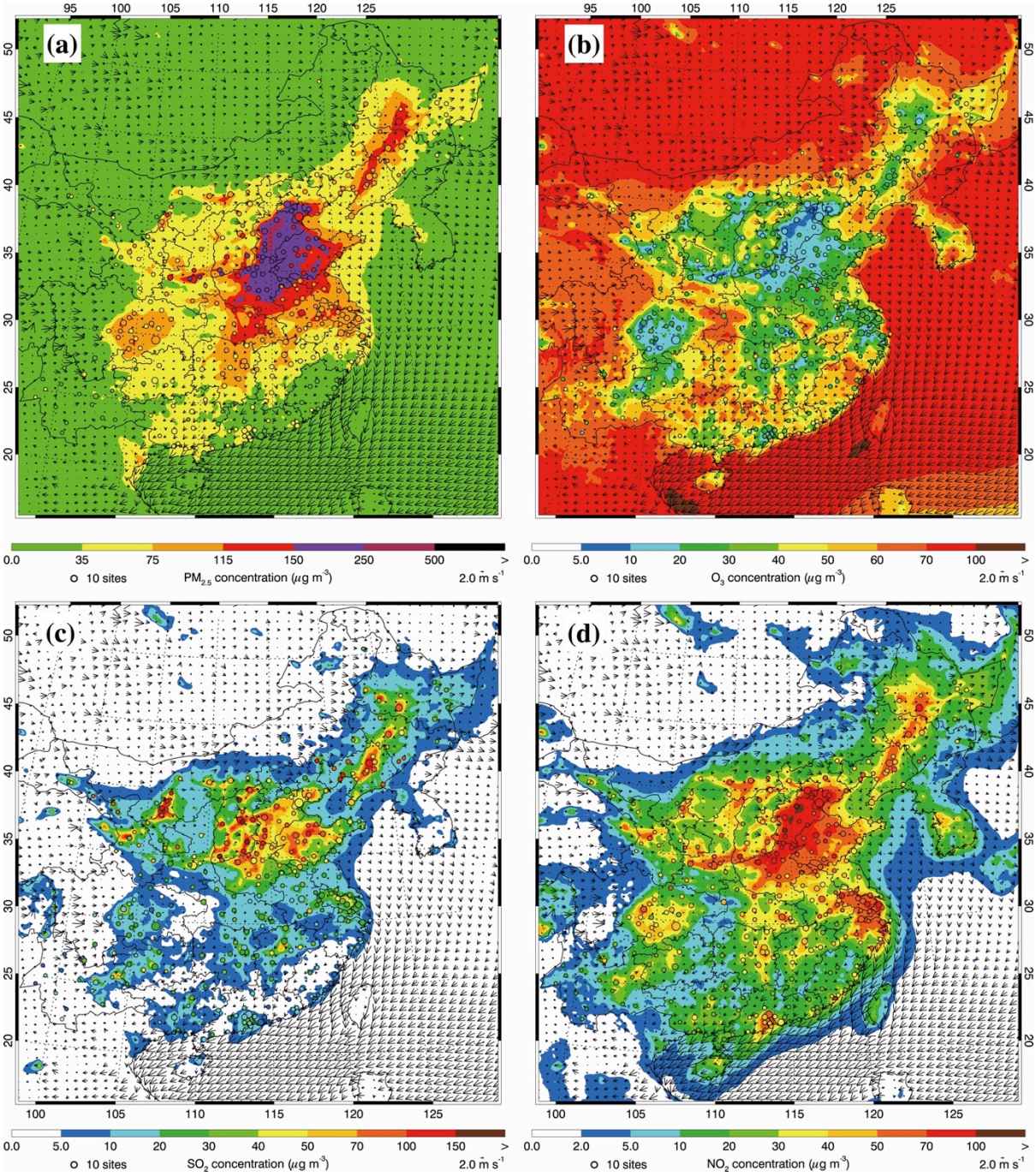

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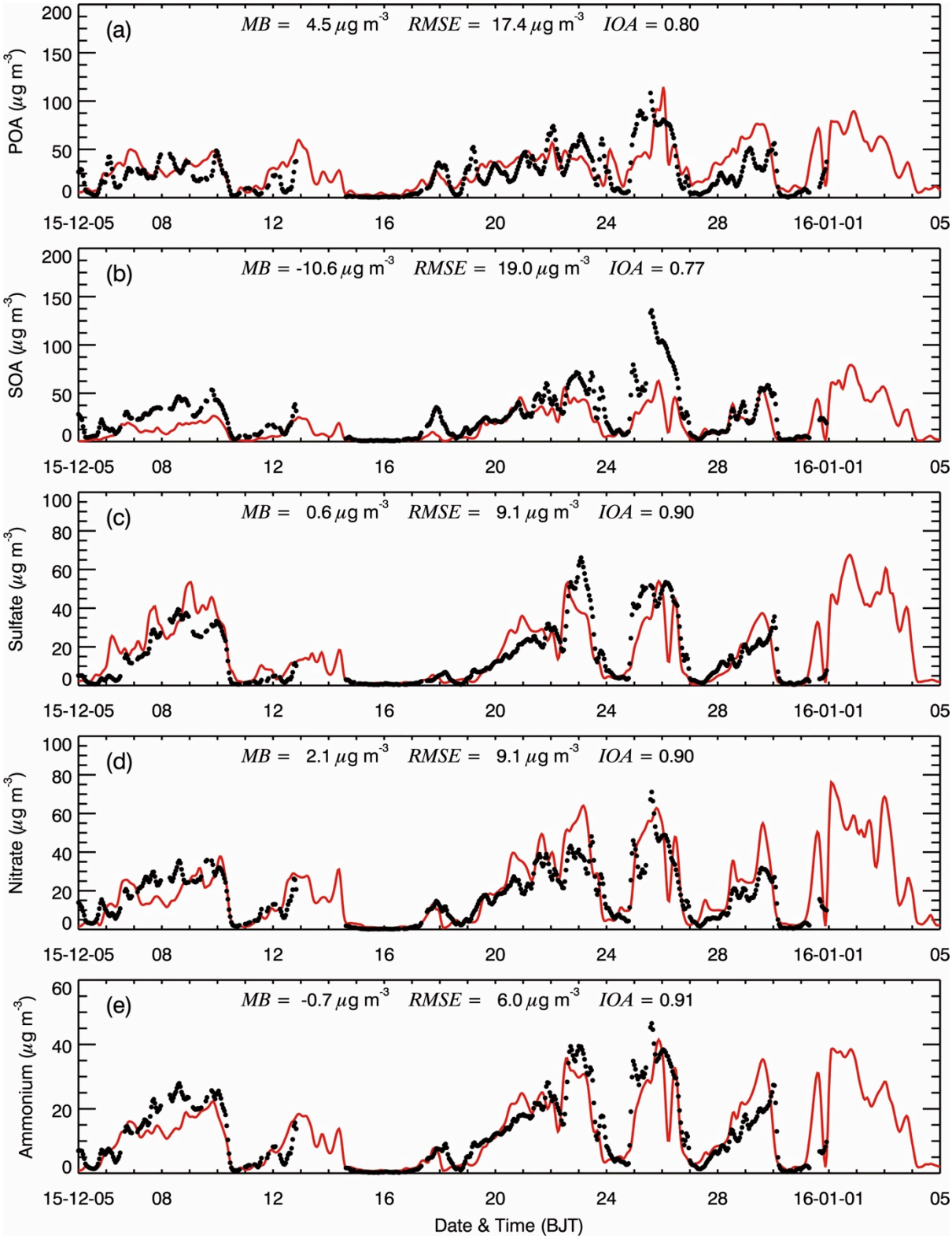

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