



Supplement of

Impacts of the heterogeneous ammonia uptake on air quality in the North China Plain

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SI. Model description and configuration

A modified version of the Weather Research and Forecasting model with Chemistry (WRF-Chem), developed by Li et al. (2010, 2011a, b), is used in this study. WRF-Chem provides the online-coupled meteorology, transport, gas-phase chemistry, photolysis, deposition, and aerosol–radiation framework. Aerosol processes are represented by the Community Multiscale Air Quality/Models-3 AERO5 modal aerosol module incorporated within WRF-Chem. AERO5 represents coagulation, condensational growth, and new-particle formation using three lognormal modes (Binkowski & Roselle, 2003). Gas-phase chemistry is represented by the Statewide Air Pollution Research Center mechanism, version 1999 (SAPRC-99). Although SAPRC-99 is older than recent SAPRC mechanisms, it is retained as part of the internally consistent model configuration and emission speciation used here. Inorganic aerosol thermodynamics are calculated using ISORROPIA version 1.7 (Nenes et al., 1998), which treats partitioning of NH_3 with sulfuric and nitric acids and ammonium-salt formation in BASE and all sensitivity simulations. The added NOCs-forming parameterization does not replace this inorganic pathway but represents an additional simplified pathway to organic nitrogen. Secondary organic aerosol (SOA), including glyoxal and methylglyoxal contributions, is represented using a volatility basis set (VBS) treatment (Li et al., 2011b). Photolysis rates are calculated with the Fast Tropospheric Ultraviolet and Visible (FTUV) radiation module (Li et al., 2005; Tie et al., 2003). Wet deposition follows the CMAQ treatment, and dry deposition follows Wesely (1989). Anthropogenic emissions for 2017 include industrial, agricultural, residential, transportation, and power-plant sectors (Li et al., 2017; Zheng et al., 2018), while biogenic emissions are calculated online with the Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther et al., 2006).

The simulations cover 1–30 November 2017, with the first 36 h discarded as spin-up. Four simulations are performed: BASE excludes the additional NOCs-forming pathway, while S(-3), S(-4), and S(-5) include the pathway with the γ values of 10^{-3} , 10^{-4} , and 10^{-5} , respectively. All simulations use identical anthropogenic emissions, meteorological and chemical initial and boundary conditions, gas-phase chemistry, aerosol treatment, and physical parameterizations. BASE is evaluated against observations, and the effects of this pathway are quantified by differentiating base case with sensitivity cases.

S2. Measurements

Model performance is evaluated using hourly fine particulate matter (PM_{2.5}), ozone (O₃), nitrogen dioxide (NO₂), and sulfur dioxide (SO₂) data from <http://www.aqistudy.cn/>. Daily filter measurements include organic carbon (OC), elemental carbon (EC), sulfate, nitrate, and ammonium at sites in and around the North China Plain (NCP). Surface ammonia (NH₃) at Xianghe is measured with a diffusive sampler (Analysts, CNR-Institute of Atmospheric Pollution, Rome, Italy; Pan et al., 2018). Nitrogen-containing organic compounds (NOCs) are quantified from high-volume PM_{2.5} filter samples at Xianghe. The measured NOCs burden is the sum of seven quantified classes—free amino acids, amines, amides, nitriles, isocyanates, urea, and cyclic NOCs (Wang et al., 2022)—and may include primary material and products from multiple secondary pathways. It is therefore used as a conservative ceiling for the modeled contribution of this pathway, not as source-resolved closure of the total atmospheric NOCs budget. NH₃ vertical column densities (VCDs) from the Infrared Atmospheric Sounding Interferometer (IASI) aboard Metop-B and Metop-C are also used. The neural-network retrieval follows Whitburn et al. (2016) and Van Damme et al. (2017). Only daytime data with relative uncertainty below 40% are retained.

We use the OC/EC ratio approach to estimate organic aerosol (OA) from filter-measured OC and EC concentrations (Strader, 1999; Cao et al., 2003, 2004). Primary organic carbon (POC), secondary organic carbon (SOC), primary organic aerosol (POA), SOA, and OA are derived as follows:

$$\text{POC} = \text{EC} \times (\text{POC/EC ratio})$$

$$\text{SOC} = \text{OC} - \text{POC}$$

$$\text{POA} = \text{POC} \times (\text{POA/POC ratio})$$

$$\text{SOA} = \text{SOC} \times (\text{SOA/SOC ratio})$$

$$\text{OA} = \text{POA} + \text{SOA}$$

Numerous studies have been performed to investigate the POA/POC and SOA/SOC ratios (Aiken et al., 2008; Yu, 2011; Yu et al., 2009), which can be used to obtain OA concentrations from measured EC and OC concentrations. In this study, the POC/EC, POA/POC, SOA/SOC ratios are assumed to be 2.4, 1.2, and 1.6, respectively, based on the previous studies (Cao et al., 2007; Aiken et al., 2008; Yu, 2011; Yu et al., 2009). It is worth to note that, these assumed values might affect the model-measurement comparisons.

Using the measured EC and OC concentrations, the SOA/EC ratio is calculated:

$$\begin{aligned} (\text{SOA/EC ratio}) &= (\text{SOA/SOC ratio}) \times (\text{SOC/EC ratio}) \\ &= (\text{SOA/SOC ratio}) \times [(\text{OC} - \text{POC}) / \text{EC}] \\ &= (\text{SOA/SOC ratio}) \times [(\text{OC/EC ratio}) - (\text{POC/EC ratio})] \end{aligned}$$

And the POA/EC ratio is derived following:

$$(\text{POA/EC ratio}) = (\text{POA/POC ratio}) \times (\text{POC/EC ratio})$$

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S3. Statistical methods for model evaluation

Four statistical metrics are used to evaluate simulated gas-phase species and aerosol components against measurements: mean bias (MB), root mean square error (RMSE), index of agreement (IOA), and correlation coefficient (R).

$$75 \quad \text{MB} = \frac{1}{N} \sum_{i=1}^N (P_i - O_i)$$

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

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

$$R = \frac{\sum_{i=1}^N [(P_i - \bar{P}) \times (O_i - \bar{O})]}{\sum_{i=1}^N (P_i - \bar{P})^2 \times \sum_{i=1}^N (O_i - \bar{O})^2}$$

Where P_i and O_i denote the concentration of predicted and observed concentration. N is the total number of
 80 predictions used for comparison, $\bar{O}$ and $\bar{P}$ are the average concentration of observation and prediction. IOA indicates the relative difference between the predicted value and the measured value with a range of 0-1. The closer IOA is to 1, the better the model performances. The R ranges from -1 to 1, with 1 implying perfect spatial consistency of observation and prediction.

85 S4. Model validation

Figure S1 presents diurnal profiles of observed and simulated near-surface $\text{PM}_{2.5}$, O_3 , NO_2 , and SO_2 concentrations averaged across monitoring sites in the NCP during November 2017. The model captures the temporal variation of $\text{PM}_{2.5}$ with an IOA of 0.93 and a small positive MB of $0.6 \mu\text{g m}^{-3}$. It reproduces the afternoon O_3 maximum and nighttime minimum, with an IOA of 0.84, although O_3 is underestimated
 90 during the first few simulation days ($\text{MB} = -1.5 \mu\text{g m}^{-3}$). NO_2 is also reasonably reproduced ($\text{IOA} = 0.83$; $\text{MB} = -1.9 \mu\text{g m}^{-3}$). SO_2 has a lower IOA of 0.67, partly because point-source emissions make its distribution sensitive to wind-field uncertainty (Bei et al., 2017).

Figure S2 shows the simulated and observed spatial distributions of mean mass concentrations of $\text{PM}_{2.5}$, O_3 , NO_2 , and SO_2 during the simulation episode. The model successfully captures the prominent $\text{PM}_{2.5}$ hotspots in
 95 southern Hebei, western Shandong, and northern Henan, where monthly mean concentrations frequently

exceeded $90 \mu\text{g m}^{-3}$ due to the synergy of intense local emissions and stagnant meteorological conditions. The spatial distributions of O_3 , NO_2 , and SO_2 are also satisfactorily reproduced, demonstrating that the simulated spatial patterns are in robust agreement with observations from ambient monitoring stations.

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Region	The North China Plain
Simulation period	1 to 30 November 2017
Domain size	300 × 300
Domain center	38°N, 116°E
Horizontal resolution	6 km × 6 km
Vertical resolution	35 vertical levels with a stretched vertical grid with spacing ranging from 30 m near the surface, to 500 m at 2.5 km and 1 km above 14 km
Microphysics scheme	WSM 6-class graupel scheme (Hong and Lim, 2006)
Cumulus scheme	Grell-Devenyi ensemble scheme (Grell and Devenyi, 2002)
Boundary layer scheme	MYJ TKE scheme (Janjić, 2002)
Surface layer scheme	MYJ surface scheme (Janjić, 2002)
Land-surface scheme	Unified Noah land-surface model (Chen and Dudhia, 2001)
Longwave radiation scheme	Goddard longwave scheme (Chou et al., 2001)
Shortwave radiation scheme	Goddard shortwave scheme (Chou and Suarez, 1999)
Meteorological boundary and initial conditions	NCEP 1°×1° reanalysis data
Chemical initial and boundary conditions	MOZART 6-hour output (Horowitz et al., 2003)
Anthropogenic emission inventory	MEIC with the base year of 2017, SAPRC-99 chemical mechanism (Li et al., 2017; Zheng et al., 2018).
Biogenic emission inventory	Online MEGAN model developed by Guenther et al. (Guenther et al., 2006)

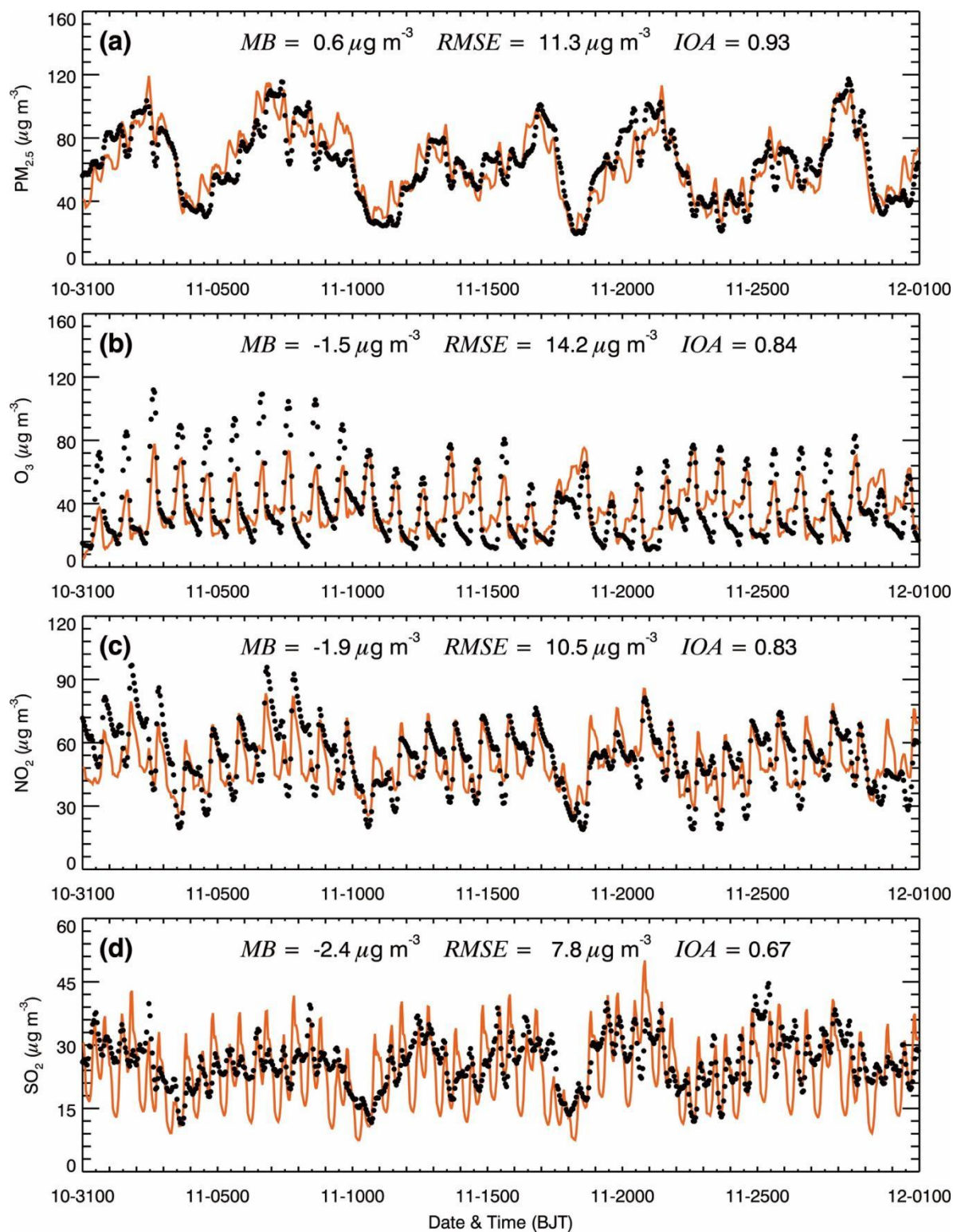


Figure S1: Diurnal profiles of observed (black dots) and simulated (solid red lines) near-surface hourly mass concentrations of (a) $\text{PM}_{2.5}$, (b) O_3 , (c) NO_2 , and (d) SO_2 averaged over all monitoring sites in the NCP in November 2017.

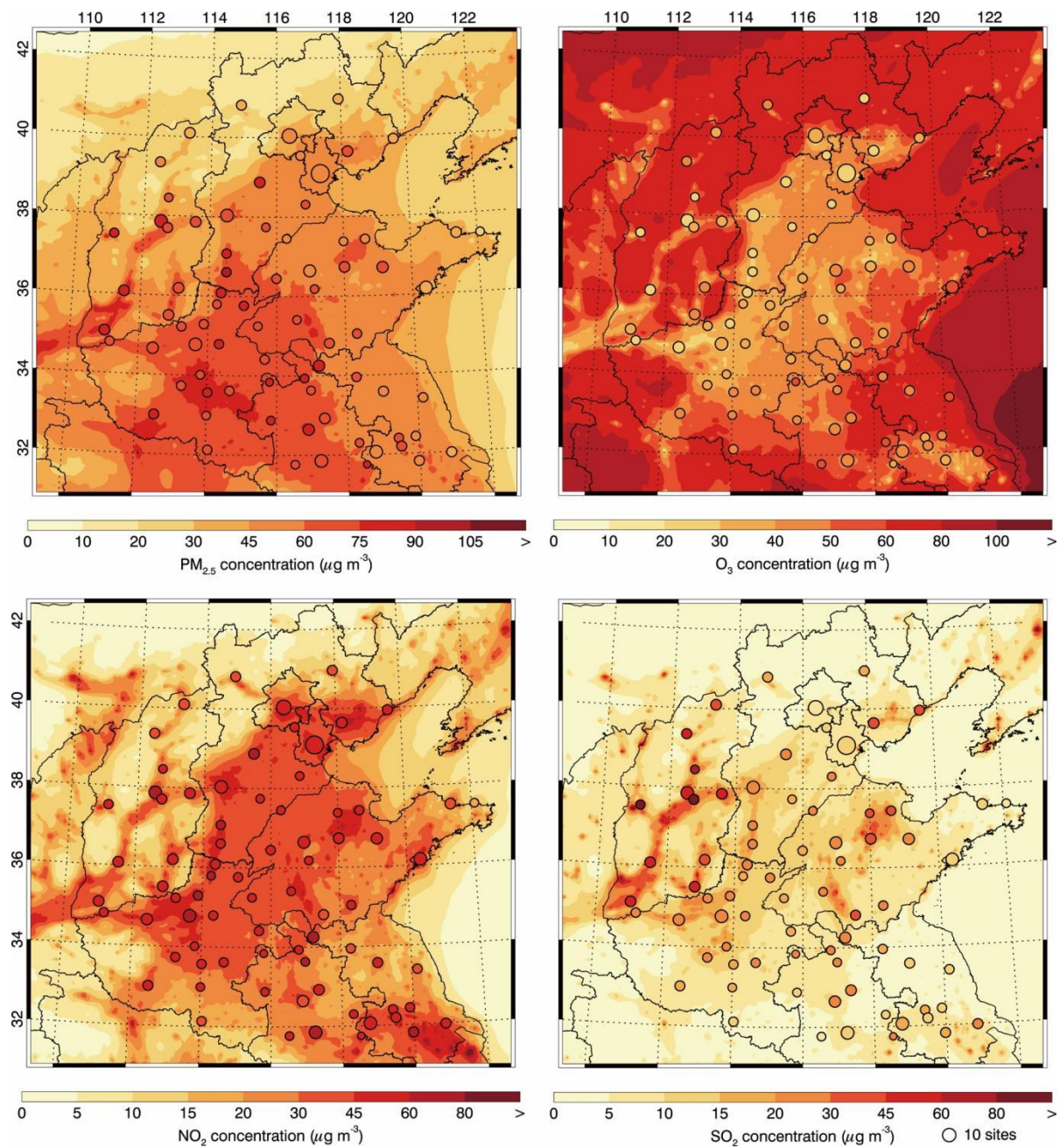


Figure S2: Pattern comparisons of simulated (color contours) versus observed (colored circles) near-surface mass concentrations of (a) $\text{PM}_{2.5}$, (b) O_3 , (c) NO_2 , and (d) SO_2 averaged in November 2017.