

Inverse modeling of SO₂ and NO_x emissions over China using multi-sensor satellite data: 1. formulation and sensitivity analysis

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Abstract. SO₂ and NO₂ observations from the Ozone Mapping and Profiler Suite (OMPS) sensor are used for the first time in conjunction with GEOS-Chem adjoint model to optimize both SO₂ and NO_x emission estimates over China for October 2013. Separate and joint (simultaneous) optimizations of SO₂ and NO₂ emissions are both conducted and compared. Posterior emissions, compared to the prior, yield improvements in simulating columnar
20 SO₂ and NO₂, in comparison to measurements from OMI and OMPS. The posterior SO₂ and NO_x emissions from separate inversions are 748 Gg S and 672 Gg N, which are 36% and 6% smaller than prior MIX emissions (valid for 2010), respectively. In spite of the large reduction of SO₂ emissions over the North China Plain, the simulated sulfate-nitrate-ammonium Aerosol Optical Depth (AOD) only decrease slightly, which can be attributed to (a) nitrate rather than sulfate as the dominant contributor to AOD and (b) replacement of ammonium sulfate with
25 ammonium nitrate as SO₂ emissions are reduced. For joint inversions, both data quality control and the weight given to SO₂ relative to NO₂ observations can affect the spatial distributions of the posterior emissions. When the latter is properly balanced, the posterior emissions from assimilating OMPS SO₂ and NO₂ jointly yield a difference of -3% to 15% with respect to the separate assimilations for total anthropogenic SO₂ emissions and ±2% for total anthropogenic NO_x emissions; but the differences can be up to 100% for SO₂ and 40% for NO₂ in some grid cells.
30 Improvements on SO₂ and NO₂ simulations from the joint inversions are overall consistent with those from separate inversions. Moreover, the joint assimilations save ~50% of the computational time than assimilating SO₂ and NO₂ separately in a sequential manner of computation. The sensitivity analysis shows that a perturbation of

NH₃ to 50% (20%) of the prior emission inventory: (a) has negligible impact on the separate SO₂ inversion, but can lead to decrease of posterior SO₂ emissions over China by -2.4% (-7.0%) in total and up to -9.0% (-27.7%) in some grid cells in the joint inversion with NO₂; (b) yield posterior NO_x emissions over China decrease by -0.7% (-2.8%) for the separate NO₂ inversion and by -2.7% (-5.3%) in total and up to -15.2% (-29.4%) in some grid cells for the joint inversion. The large reduction of SO₂ between 2010 and 2013, however, only leads to ~10% decrease of AOD regionally; reducing surface aerosol concentration requires the reduction of emissions of NH₃ as well.

1. Introduction

Both SO₂ and NO₂ in the atmosphere have adverse impacts on human health and can affect radiative forcing that leads to climate change. Not only do they cause inflammation and irritation of the human's respiratory system, but they also react with other species to form sulfate and nitrate aerosols (Seinfeld and Pandis, 2016), which subsequently can lead to or exacerbate respiratory and cardiovascular diseases (Lim et al., 2012). Sulfate and nitrate account for the largest mass of anthropogenic aerosols, which contributed to ~3 million premature deaths worldwide in 2010 (Lelieveld et al., 2015). In addition to the health impacts, anthropogenic sulfate and nitrate particles are estimated to have caused -0.4 and -0.15 W m⁻² radiative forcing, respectively, on a global scale between 1750 and 2011 through scattering solar radiation, and via modifying cloud microphysical properties (Myhre et al., 2013).

Satellite-derived global distributions of SO₂ and NO₂ Vertical Column Densities (VCDs) have been used to study the aforementioned impacts of SO₂ and NO₂ on atmospheric composition, climate change, and human health. In particular, since SO₂ and NO₂ VCDs are, to first order, linearly related to SO₂ and NO_x emissions (Calkins et al., 2016), they can be used to update bottom-up emission inventories that have large uncertainties and a temporal lag often of at least one year (Liu et al., 2018). Of particular interest for this study is China, which has large SO₂ and NO_x emissions from anthropogenic sources (coal-fired power plants, industry, transportation, and residential activity). Moreover, China has seen a 62% reduction in anthropogenic SO₂ emissions and a 17% reduction of anthropogenic NO_x emissions on average from 2010 to 2017 (Zheng et al., 2018) due to the implementation of emission control policies, and these changes vary by regions, cities (Liu et al., 2016), and sectoral sources (Zheng et al., 2018). The reduction of SO₂ emissions mainly occurred in the coal-fired power plants and industries while the decrease of NO_x emissions was largely ascribed to coal-fired power plants (Zheng et al., 2018). Noticeable uncertainties larger than 30% for both anthropogenic SO₂ and NO_x in 2010 over China were documented (Li et

al., 2017b) and can be larger at the regional scale due to the uncertainty of activity rates, emission factors, and spatial proxies, which are used in the bottom-up approach (Janssens-Maenhout et al., 2015). The uncertainty is large and can be compounded by possible discrepancies caused by the temporal lag of bottom-up emission
65 inventories and the rapid changes of emissions over time.

Several methods have been developed to update SO₂ and NO_x emissions using satellite VCD retrievals of SO₂ and NO₂, which have global coverage and allows near-real-time access. The mass balance method, which scales
70 prior emissions by the ratios of observed VCDs to Chemistry Transport Model (CTM) counterparts, was applied to SO₂ retrievals from SCanning Imaging Absorption SpectroMeter for Atmospheric CHartographY (SCIAMACHY) and Ozone Monitoring Instrument (OMI) (Lee et al., 2011;Koukouli et al., 2018) and to NO₂ from Global Ozone Monitoring Experiment (GOME) and OMI (Martin et al., 2003;Lamsal et al., 2010) to estimate SO₂ and NO_x emissions, respectively. Lamsal et al. (2011) simulated the sensitivity of VCDs to emissions
75 (the finite difference mass balance approach) using a CTM, which was applied to OMI NO₂ retrievals to estimate NO_x emissions. SO₂ VCD retrievals from GOME, GOME-2, SCIAMACHY, and Ozone Mapping and Profiler Suite (OMPS) were used to estimate point sources through linear regression between VCDs and emissions or function fitting, although the method can only detect about half of the total anthropogenic SO₂ emissions (Li et al., 2017a;Zhang et al., 2017;Fioletov et al., 2013;Fioletov et al., 2016). With explicit considerations of chemistry,
80 transport, and deposition, the four-dimension variational data assimilation (4D-Var) approach was applied to estimate emissions using SO₂ data from OMI (Wang et al., 2016;Qu et al., 2019a), and NO₂ data from SCIAMACHY, GOME-2, and OMI (Kurokawa et al., 2009;Qu et al., 2017;Kong et al., 2019). The 4D-Var posterior has a smaller root mean square error than the mass balance posterior, especially in the conditions when the initial guess and true emissions have different spatial patterns (Qu et al., 2017); this is because the spatial extent of
85 source influences on modelled column concentrations (Turner et al., 2012) are only indirectly and partially accounted for in the mass balance approach. Cooper et. al (2017), however, showed that the iterative finite difference mass balance approach has similar normalized mean error value as the 4D-Var approach for global-scale models with coarse resolution when synthetic NO₂ columns observations are used to constrain NO_x emissions. To combine the strengths of the 4D-Var and mass balance approaches, Qu et al. (2017) further
90 introduced a hybrid 4D-Var-mass-balance approach, which can better capture trends and spatial variability of NO_x emissions than the mass balance approach and save significant computational resources when applied to constrain monthly NO_x emissions for multiple years. Other data assimilation approaches including the ensemble Kalman

filter method (Miyazaki et al., 2012;Miyazaki et al., 2017) and the Daily Emission estimates Constrained by Satellite Observation (DECISO) algorithm (Mijling and van der A, 2012;Ding et al., 2015) have also been used to
95 constrain NO_x emissions.

Here, we focus on the development and feasibility for joint 4D-var assimilation of satellite-based SO₂ and NO₂ data to optimize SO₂ and NO_x emission strengths simultaneously. Specifically, this study aims to conduct 4D-Var assimilation of VCDs of SO₂ and NO₂ from OMPS to constrain SO₂ and NO_x emissions over China using the
100 GEOS-Chem 4D-Var inverse modeling framework. In our companion study (Wang et al., 2019), we develop approaches to downscaling the optimized emission inventories for improving air quality predictions. Despite their numerous applications for top-down estimate of SO₂ and NO_x emissions in the past two decades, GOME and SCIAMCHY stopped providing data in 2004 and 2012, respectively, while OMI has been suffering from a row anomaly that leads to much less spatial coverage and larger data uncertainty (Schenkeveld et al., 2017). Hence, it
105 is important to study the potential of next-generation sensors such as OMPS toward continuously monitoring the change of SO₂ and NO_x emissions and their atmospheric loadings. Two OMPS sensors onboard Suomi NPP and NOAA-20 have been launched in 2011 and 2018, respectively, and the third one is expected to be launched in 2020. As OMPS will continue to provide SO₂ and NO₂ retrievals in the next two decades, this study, for the first time, seeks to provide a critical assessment of the extent to which the OMPS observations improve emissions
110 estimates and air quality forecast at the regional scale.

The novelty of this study lies not only in the first application of OMPS SO₂ and NO₂ retrievals to constrain emissions using the 4D-Var technique but also in the deployment of OMI data to assess the GEOS-Chem simulation with posterior emissions, thereby studying the degree to which OMPS and OMI retrievals, despite their
115 difference in sensor characteristics and inversion techniques, can provide consistent constraints for the model improvement. Qu et al. (2019a) showed that posterior SO₂ emissions derived from different OMI SO₂ products vary in strength and have consistent trend signs. Our study here using OMPS thus examines an important issue, which is whether or not there would be any artificial trends in our climate data record of atmospheric SO₂ and NO₂ due to the transition of satellite sensors (Wang and Wang, 2020). Our study is also different from past studies
120 (Wang et al., 2016;Qu et al., 2017;Qu et al., 2019a;Qu et al., 2019b) that have applied the 4D-Var technique to OMI data with the GEOS-Chem adjoint model, but did not include evaluation with independent satellite data. Qu et al. (2019b) showed joint inversion using OMI SO₂ and NO₂ benefits from simultaneous adjustment of OH and O₃ concentrations, which supports assimilating OMPS SO₂ and NO₂ observations simultaneously in this study.

125 Additionally, considering that the uncertainty of NH₃ emission inventories is up to 153% over China (Kurokawa
et al., 2013) and NH₃ emissions are not constrained in our inversions, we also explore issues related to the co-
variation among species that appear to be independent but indeed are connected through chemical processes and
analyze the differences in responses of emissions and aerosols to NH₃ emissions uncertainty between joint and
single-species assimilations. Finally, this paper also provides the foundation for the Part II investigation (Wang
et al., 2019) in which we develop various downscaling methods to illustrate that optimized emission, albeit its
130 coarse resolution inherent from OMPS data, can be used to improve the air quality forecast at the resolution much
finer than OMPS pixel size.

We describe OMPS and OMI data in Sect. 2. The GEOS-Chem model and its adjoint as well as the design of
numerical experiments are presented in Sect. 3. Results of case studies for October 2013 are provided in Sect. 4.
135 Sect. 5 consists of discussion and conclusions.

2. Data

2.1 OMPS data as constraints

We use OMPS Level-2 SO₂ and NO₂ tropospheric VCDs in October 2013 as constraints to optimize SO₂ and NO_x
emissions over China. The OMPS nadir mapper on board the Suomi-NPP satellite, launched in November 2011,
140 observes hyperspectral solar radiance and earthshine radiance at 300-380 nm (Flynn et al., 2014). With 35
detectors of 50x50 km nominal pixel size in cross-track direction, OMPS has a swath of 2800 km flying across
the equator at 1:30 PM local time ascendingly at the sunlit side of the Earth surface and providing global coverage
daily. Both SO₂ and NO₂ are retrieved through the Direct Vertical Column Fitting (DVCF) algorithm with SO₂
and NO₂ atmospheric profile information from GEOS-Chem simulations and have a retrieval precision of 0.2 DU
145 and 0.011 DU, respectively, which are estimated from the standard background (a clean region that is far from
emission sources) retrievals (Yang et al., 2013; Yang et al., 2014). These precision values can be used as the
observation error in the cost function of data assimilation. However, we should notice that the estimated
observation (retrieval) errors only represent the observation error distribution of the products as a whole; it cannot
represent the observation error distribution for every pixel, because the pixel-level error is amenable to
150 spatiotemporal change of cloud fraction, satellite observation geometry, aerosol impacts, etc. In theory, if the
uncertainties can be analytically described at the pixel level, they would be directly applied to improve the satellite
product in the first place.

Only pixels with both Solar Zenith Angle (SZA) and View Zenith Angle (VZA) less than 75° are used, as larger
155 SZA or VZA result in longer light path length, and consequently less information content and lower data quality
for retrieving the change of SO₂ or NO₂ loadings in the Plane Boundary Layer (PBL) where the two trace gases
from anthropogenic sources mainly concentrate. We also remove the pixels with Radiative Cloud Fraction (RCF)
larger than 0.2 for SO₂ and 0.3 for NO₂ as a trade-off between the data amount and cloud impacts. Considering
their large uncertainty, OMPS SO₂ retrievals in the grid cell where the prior simulation is less than 0.1 DU will
160 not be used, except in Quality Control (QC) sensitivity analysis experiments.

2.2 OMI data for assessment

OMI Level-3 SO₂ and NO₂ tropospheric VCDs at a spatial resolution of $0.25^\circ \times 0.25^\circ$ from NASA are used for
evaluating the model results. OMI is a UV-vis hyperspectral sensor that observes solar irradiance and earthshine
radiance at 300-500 nm. The swath of OMI is 2600 km, consisting of 60 detectors with the nominal pixel size of
165 13×24 km² at nadir. OMI flies across the equator in the ascending node at 1:45 PM local time, which is very close
to the 1:30 PM local time for OMPS. Due to row anomaly (Schenkeveld et al., 2017), OMI takes more than one
day to provide global coverage. The Level-3 product is derived from the Level-2 product; the latter is retrieved
through the Principal Component Analysis (PCA) algorithm with a fixed Air Mass Factor (AMF) assumption for
SO₂ (Li et al., 2013) and variation of the Differential Optical Absorption Spectroscopy (DOAS) algorithm for
170 NO₂ (Krotkov et al., 2017; Marchenko et al., 2015), with a precision of 0.5 DU (Li et al., 2013) and 0.017 DU
(Krotkov et al., 2017), respectively. In the Level-3 product, pixels affected by row anomaly are removed. For SO₂,
only the pixel with the shortest light path, SZA less than 70° , RCF less than 0.2, and detector number in the range
of 2 to 59 (1-based) is retained in a $0.25^\circ \times 0.25^\circ$ grid cell and then corrected with a new AMF based on GEOS-
Chem SO₂ profile simulation (Leonard, 2017). For the OMI Level-2 NO₂ product, the AMF calculation is based
175 on Global Modeling Initiative NO₂ profile simulation (Krotkov et al., 2017), and all pixels with SZA less than
 85° , terrain reflectivity less than 0.3, RCF less than 0.3 are averaged in a $0.25^\circ \times 0.25^\circ$ grid cell weighted by the
overlapping area of grid cell and pixel to form Level-3 product (Bucsela et al., 2016). In the assessments, OMI
observations are averaged at $2^\circ \times 2.5^\circ$ model grid cell, and model simulations are sampled by OMI observational
time.

180 3. Method

3.1 GEOS-Chem and its adjoint

GEOS-Chem is a 3-D chemistry transport model driven by emissions and GEOS-FP meteorological fields. The secondary sulfate-nitrate-ammonium aerosol formation in the model is introduced by Park et al. (2004). Both aerosols and gases are removed by wet deposition, including washout and rainout from large-scale or convective precipitation (Liu et al., 2001) and the dry deposition following a resistance-in-series scheme with aerodynamic resistance and boundary resistance calculated from GEOS-FP meteorological field and surface resistances based largely on a canopy model (Wang et al., 1998; Wesely, 1989). Anthropogenic SO₂, NO_x, and NH₃ emissions used over East Asia are the mosaic emission inventory (MIX) (Li et al., 2017b) for year 2010. SO₂ and NO₂ VCDs are simulated at 2°x2.5° resolution with 47 vertical layers using both the prior and posterior emission inventories to compare with OMI retrievals.

The GEOS-Chem adjoint model is a tool for efficiently calculating the sensitivity of a scalar cost function with respect to large numbers of model parameters simultaneously such as emissions (Henze et al., 2007). In this study, the cost function is defined as Eq. (1).

$$J(\boldsymbol{\sigma}) = \gamma \frac{1}{2} [\mathbf{H}_{\text{SO}_2}(\mathbf{M}(\boldsymbol{\sigma})) - \mathbf{c}_{\text{SO}_2}]^T \mathbf{S}_{\text{SO}_2}^{-1} [\mathbf{H}_{\text{SO}_2}(\mathbf{M}(\boldsymbol{\sigma})) - \mathbf{c}_{\text{SO}_2}] + \frac{1}{2} [\mathbf{H}_{\text{NO}_2}(\mathbf{M}(\boldsymbol{\sigma})) - \mathbf{c}_{\text{NO}_2}]^T \mathbf{S}_{\text{NO}_2}^{-1} [\mathbf{H}_{\text{NO}_2}(\mathbf{M}(\boldsymbol{\sigma})) - \mathbf{c}_{\text{NO}_2}] + \frac{1}{2} [\boldsymbol{\sigma} - \boldsymbol{\sigma}_a]^T \mathbf{S}_a^{-1} [\boldsymbol{\sigma} - \boldsymbol{\sigma}_a] \quad (1)$$

\mathbf{E} is a vector in which SO₂ and NO_x emissions are ordered by GEOS-Chem model grid cell and by species. \mathbf{E}_a is a prior estimate, and $\boldsymbol{\sigma}$ is a state vector, consisting of $\ln(\mathbf{E}_i/\mathbf{E}_{a,i})$, where E_i and $E_{a,i}$ are the i th element in \mathbf{E} and \mathbf{E}_a , respectively. \mathbf{c}_{SO_2} and \mathbf{c}_{NO_2} are vectors of OMPS SO₂ and NO₂ tropospheric VCDs, respectively. \mathbf{S}_{SO_2} and \mathbf{S}_{NO_2} are observation error covariance matrixes for SO₂ and NO₂ and are assumed to be diagonal, which means observational errors are uncorrelated. \mathbf{M} is the GEOS-Chem model that simulates the relationship between SO₂ and NO₂ concentrations in the atmosphere and the emissions factors. \mathbf{H}_{SO_2} and \mathbf{H}_{NO_2} are observation operators which map GEOS-Chem simulations of SO₂ and NO₂ to the observational space, respectively. $\boldsymbol{\sigma}_a$ is the prior estimate of $\boldsymbol{\sigma}$, and \mathbf{S}_a is the error covariance matrix for $\boldsymbol{\sigma}_a$. \mathbf{S}_a is assumed to be diagonal with a relative error of 50% for SO₂ and 100% for NO_x as used in Xu et al. (2013). γ is a parameter we introduce to balance the importance of the SO₂ observation term (first term on the right side of Eq. (1)) and NO₂ observational term (second term on the right side of Eq. (1)), given both the different sizes and observation errors of these two observation datasets.

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OMPS SO₂ and NO₂ tropospheric VCDs are directly compared to GEOS-Chem tropospheric VCDs of SO₂ ($H_{\text{SO}_2}(\mathbf{M}(\boldsymbol{\sigma}))$ in Eq. (1)) and NO₂ ($H_{\text{NO}_2}(\mathbf{M}(\boldsymbol{\sigma}))$ in Eq. (1)). Retrieving satellite SO₂ and NO₂ tropospheric VCDs requires assumptions regarding SO₂ and NO₂ vertical profiles, as the sensitivity of the radiance observed by satellite sensors to the changes of SO₂ or NO₂ loadings is a function of plume height. If the vertical profile assumptions in the retrieval process are inconsistent with the GEOS-Chem simulations, the inconsistency partly contributes to the difference between the GEOS-Chem simulations and the OMPS retrievals ($H_{\text{SO}_2}(\mathbf{M}(\boldsymbol{\sigma})) - \mathbf{c}_{\text{SO}_2}$ or $H_{\text{NO}_2}(\mathbf{M}(\boldsymbol{\sigma})) - \mathbf{c}_{\text{NO}_2}$). In this study, OMPS SO₂ and NO₂ tropospheric VCDs are retrieved using the shape of vertical profiles from GEOS-Chem simulations (Yang et al., 2013; Yang et al., 2014), but the differences of model version, simulation year, and emission inventory still exist. These differences still can lead to the differences of vertical profiles, hence partly contributing to the difference between the GEOS-Chem simulations and the OMPS retrievals. The vertical profile differences can lead to a mean bias of -6.8% overall at the pixel level (Fig. S1) and -7.5% (Fig. S2) for OMPS SO₂ and NO₂ retrievals, respectively. And we shall discuss the impacts of these bias on emission inverse modeling in Sect. 4.1.1.

225 In the optimization formulation, the forward model errors are also considered as part of the observation error term. However, while several ways to construct model error covariance matrix exist, including the Hollingworth-Lönnerberg (Hollingsworth & Lönnerberg, 1986) and NMC (Bannister, 2008) methods, their application for off-line CTM model error characterization deserves a separate a study. The Hollingsworth method extracts observation error variance (including forward model error) from (observation – background) covariance statistics with the assumptions that observation error is spatially uncorrelated, background error is spatially correlated as a function of distance, and observation error and background error are uncorrelated. The assumption that background error is spatially correlated as a function of distance only is suitable for the meteorological fields that vary smoothly, but for chemical species, emissions also contribute significantly to model errors and emissions are spatially correlated. The NMC method is normally applied to weather forecast models or on-line-coupled weather-chemistry models (Benedetti and Fisher, 2007). Off-line CTMs such as GEOS-Chem use the meteorological reanalysis and so, NMC is not applicable here to quantify the CTM’s transport error. Consequently, CTM’s transport errors are neglected in the past emission optimization work (Wang et al., 2016) and are adopted in this study. Admittedly, this simplification should be studied in future together with the evaluation and developments of methods to characterize off-line CTM errors.

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We developed the observation operators for OMPS SO₂ and NO₂, and the validations are shown in Fig. 1. The sensitivities of the cost function with respect to anthropogenic SO₂ and NO_x emissions from the adjoint model is consistent with the sensitivities calculated through the finite difference approach. Hence, Fig. 1 confirms the correctness of the new observation operators integrated into the GEOS-Chem adjoint model.

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To optimize the emission inventories, σ is adjusted iteratively until the cost function is minimized. The minimization is conducted with the L-BFGS-B algorithm (Byrd et al., 1995), which utilizes the sensitivity of the cost function with respect to σ that is calculated by the GEOS-Chem adjoint model. The minimization process halts when the difference in the cost function between two consecutive iterations is less than 3%. This selection is to expediate the computation while still maintain the similar accuracy for the optimization; further tests show that the more iterations (after <3% reduction of cost function) doesn't yield discernable difference in the cost function values (Fig. S3) and optimization results (Table S1 and S2).

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3.2 Experiment design

Several elements play a role in the inverse modeling of emissions, including data quality control, balancing the spatial distributions of observational frequencies for the same species, balancing the observation contributions from different species, and uncertainties in the NH₃ emission inventory (because NH₃ has impacts on SO₂ and NO₂ lifetimes). To investigate the impacts of these factors on the posterior emissions, we design a set of experiments as summarized in Table 1 and Table 2. All these experiments use OMPS SO₂ and NO₂ retrievals to optimize corresponding emissions over China in October 2013 at a horizontal resolution of 2°×2.5°. Although finer resolution options such as 0.5°×0.625° or 0.25°×0.3125° are available for China, the 2°×2.5° resolution is selected for two reasons: (1) Save computational time; (2) chiefly, the coarse resolution of OMPS retrievals (50 km × 50 km at nadir and 190 km × 50 km at edges) has no first-order information to resolve the emissions at fine-resolution of 0.5°×0.625° or 0.25°×0.3125°. In Part II (Wang et al., 2019) of this study, we develop downscaling tools for regional air quality modeling. Indeed, one of the goals of the two-part investigation is to illustrate how OMPS data could be used to improve the air quality forecast at the resolution much finer than OMPS pixel size.

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3.2.1 Control experiments

The first control experiment is E-SO₂ (Table 1), in which only OMPS SO₂ tropospheric VCDs are used to constrain SO₂ emissions by removing the second additive term on the right side of Eq. (1). Consequently, γ is set

to unity. If the OMPS SO₂ tropospheric VCD error is set to 0.2 DU (Yang et al., 2013) for every pixel, the SO₂ observational term in the cost function (first term on the right side of Eq. (1)) over the North China Plain is much larger than that over Southwestern China (Fig. 2b), which yield high possibility to over-constrain the former and under-constrain the latter. The spatially unbalanced cost function is caused by cloud screening, as the number of observations over Southwestern China is much less than that over the North China Plain (Fig. 2a). To balance the cost function by accounting for this difference in the number of observations, SO₂ observation error is set to 0.2 DU multiplied by the square root of the number of OMPS overpasses that have SO₂ observation in the 2°x2.5° GEOS-Chem grid cell. The balance approach essentially normalizes observation terms in the cost function by the observation counts, which has been used in our study (Xu et al., 2015) to optimally invert aerosol optical properties from the skylight polarization and intensity measurements by AERosol RObotic NETwork (AERONET).

In the second experiment, E-NO₂, OMPS NO₂ tropospheric VCDs alone are used to constrain NO_x emissions by removing the first additive term on the right side of Eq. (1). Due to cloud screening, much more OMPS NO₂ observations exist over the North China Plain than over Southwestern China, which also could lead to a spatially unbalanced cost function if the OMPS NO₂ observation error is uniform. The OMPS NO₂ observation error is, however, assumed to be 0.011 DU (Yang et al., 2014) for every pixel in this study, regardless of location, because the NO_x emissions adjustments during the inverse modeling process are supposed to be mainly over the North China Plain where prior NO_x emissions are much larger than those over Southwestern China. In this study, we optimize emission scale factors rather than the emissions themselves. As a result, emissions are adjusted mainly at locations where prior emissions are large and kept as zero for those (2°x2.5°) grid boxes of zero prior emissions.

In the third experiment, E-joint, both the SO₂ and NO₂ from OMPS are used simultaneously for two reasons. Firstly, SO₂ and NO₂ concentrations can affect each other through several pathways. For example, Qu et. al (2019b) showed that the change of SO₂ or NO_x emissions lead to the changes of O₃ and OH concentrations, hence the changes of SO₂ and NO₂ oxidations. Here, we will explore how the optimization results may dependent on the uncertainty of ammonia emissions (as elaborated in Sect. 3.2.2). Secondly, the computational time is reduced by ~50% in the joint assimilation as compared to separate assimilations when computational resource are restricted to running individual inversions sequentially (as opposed to in parallel), and energy usage is also saved; the latter require the realization of GEOS-chem adjoint twice, while only once is needed by the former.

In the E-joint experiment, observational terms for SO₂ and NO₂ in the cost function should be balanced through setting γ in Eq. (1). When it is not balanced, SO₂ observations have very little impact on the inversion results as the optimization algorithm will firstly minimize the observational term for NO₂ unless many more iterations than is computationally feasible are performed, which is caused by the fact that observational error and valid number of NO₂ observation are respectively smaller and larger than the counterparts of SO₂. We thus subjectively derive γ in a non-arbitrary way in order to focus equally on both species, thereby tackling the imbalance in their observational constraints. In this manner, the cost function is defined to serve the purpose of joint inversion of SO₂ and NO₂ emissions. Initially, we set γ to be the ratio of number of NO₂ observations to the number of SO₂ observations. This approach is not feasible here as the SO₂ observational error in E-SO₂ is much larger than the NO₂ observational error in E-NO₂; not only does the number of observations play a role, but the observation error also has important impacts on balancing the cost function. If γ is simply set as unity, the NO₂ observational term in Eq. (1) is a factor of ~200 larger than the SO₂ observational term, which can lead to OMPS SO₂ in the E-joint experiment to be negligible. Consequently, to balance the two terms, γ is set as 200 (ratio of observational term in E-NO₂ to that in E-SO₂) in E-joint and sensitivity experiments of using different values of γ are conducted (see section 3.2.2). Similar balance approach that adjusts contribution of observation terms in the cost function is used in the past work that assimilates satellite trace gas retrievals to invert emissions (Qu et al., 2019b) or invert the aerosol optical properties from skylight polarization measurements of AERONET (Xu et al., 2015).

3.2.2 Sensitivity experiments

To investigate the impacts of data quality control and spatially balancing the cost function on optimizing SO₂ emissions only, we design two sensitivity experiments. The first is E-SO₂-noQC-noBL that is similar to E-SO₂ except that: (1) OMPS SO₂ retrievals in the 2°x2.5° grid cell where the prior GEOS-Chem simulation is less than 0.1 DU are also assimilated, i.e. without QC; (2) OMPS SO₂ observation error is set as 0.2 DU for every pixel, which means we do not spatially balance the cost function. The second sensitivity experiment is E-SO₂-noBL in which the cost function is not spatially balanced, and it uses the same setting as E-SO₂ except for assuming an observation error of 0.2 DU uniformly.

To evaluate the effect of γ (of 200) in E-joint, we further test γ values of 20, 50, 100, 300, 500, 1000, 1500, and 2000 in the joint inversions; hereafter these experiments are named E-joint-d γ . Through these sensitivity experiments, we study the proper γ range for jointly assimilating OMPS SO₂ and NO₂. In future studies that may be conducted to jointly assimilate OMPS SO₂ and NO₂ for other months to obtain a long-term optimized emission

inventory, it is proposed to set proper γ values for each month based on the range with easy adjustment according
 330 to the numbers of OMPS SO₂ and NO₂ observations and their associated errors.

NH₃ emissions are not optimized in our inverse modeling and yet their uncertainty is up to 153% over China
 (Kurokawa et al., 2013). Thus, it is important to evaluate how this uncertainty may affect posterior SO₂ and NO_x
 emissions. Wang et al. (2013) emphasized the importance of controlling NH₃ to alleviate PM_{2.5} pollution over
 335 China, however it could worsen acid rain (Liu et al., 2019). Changes of NH₃ emissions is expected to change
 ammonium and nitrate aerosol concentrations, or the aerosol surface area for heterogeneous N₂O₅ chemistry,
 hence affecting NO₂ concentrations or posterior NO_x emissions in the inverse modeling. The change of posterior
 NO_x emissions is expected to lead to the change of posterior SO₂ emissions in the joint inverse modeling. Thus,
 we shall investigate if NH₃ emissions are reduced to 50% and 20%, how the optimized SO₂ and NO₂ emission
 340 inventories would change. Correspondingly, all these experiments are summarized in Table 2. E-SO₂-0.5NH₃, E-
 NO₂-0.5NH₃, and E-joint-0.5NH₃- γ 500 in Table 2 are similar to E-SO₂, E-NO₂, and E-joint- $d\gamma$ ($\gamma=500$) in Table
 1, respectively, but NH₃ emissions are set to 50% of the original values. Similarly, E-SO₂-0.2NH₃, E-NO₂-0.2NH₃,
 and E-joint-0.2NH₃- γ 500 are the scenarios that NH₃ emissions are set to 20% of the original values.

3.3 Evaluation statistics

We use linear correlation coefficient (R), root mean square error (RMSE), mean bias (MB), normalized mean bias
 (NMB), normalized standard deviation (NSD), and normalized centered root mean square error (NCRMSE) as
 measures to evaluate GEOS-Chem SO₂ and NO₂ VCD simulations with satellite (OMPS and OMI) observations.
 NSD is the ratio of the standard deviation of the simulation to the standard deviation of the observation. NCRMSE
 is similar to RMSE, but the impact of bias is removed. This is shown in Eq. (2), where i is the i th grid cell, N is
 350 the total number of grid cells, M_i and O_i are the i th GEOS-Chem simulation and satellite observation, respectively,
 and \bar{M} and \bar{O} are averages of GEOS-Chem simulation and satellite observation, respectively. A composite
 summary of these statistics is provided by the Taylor diagram (Taylor, 2001) which is a quadrant which
 summarizes R (shown as cosine of polar angle), NSD (shown as radius from the quadrant center), and NCRMSE
 (shown as radius from expected, satellite observation, point, which is located at the point where R and NSD are
 355 unity).

$$\text{NCRMSE} = \frac{\sqrt{\frac{1}{N} \sum_{i=1}^N [(M_i - \bar{M}) - (O_i - \bar{O})]^2}}{\sqrt{\frac{1}{N} \sum_{i=1}^N (O_i - \bar{O})^2}} \quad (2)$$

4. Results

4.1 Separate and joint assimilations of SO₂ and NO₂

4.1.1 Self-consistency check

360 The cost functions are reduced by 41.6%, 27.6%, and 28.6% for E-SO₂, E-NO₂, and E-joint, respectively, and the results are shown in Fig. 3. Noticeably, hot spots of SO₂ VCDs over the North China Plain and the Sichuan Basin are shown in the OMPS observations (Fig. 3a), prior (Fig. 3b), posterior E-SO₂ (Fig. 3c), and posterior E-joint (Fig. 3d) simulations, however the prior simulation has an NMB of 106.5% (Fig. 3i) when compared with OMPS. The SO₂ NMB (106.5%) between GOES-Chem prior simulation and OMPS is much larger than the NMB (-6.8%,
365 Fig S1) caused by the difference of SO₂ vertical profiles between OMPS SO₂ retrieval algorithm and current prior simulation; thus averaging kernel is not considered in the OMPS SO₂ observation operator. This large positive NMB decreases to 13.0% and 38.3% in the posterior E-SO₂ (Fig. 3j) and E-joint (Fig. 3k) simulations with an RMSE decreasing from 0.42 DU to 0.13 DU and 0.20 DU and R increasing from 0.62 to 0.72 and 0.64, respectively. Large NO₂ values are found over the North China Plain and Eastern China with large NO_x emissions
370 from the transportation sector (Fig. 3e-h). Comparing with OMPS NO₂, GEOS-Chem results have an RMSE of 0.05 DU in the prior simulation (Fig. 3l) and reduce to 0.02 DU and 0.03 DU for E-NO₂ (Fig. 3m) and E-joint (Fig. 3n), with R increasing from 0.95 to 0.99 and 0.98, respectively.

Similarly, the averaging kernel is not considered in the OMPS NO₂ observation operator for optimization for the
375 following reasons. First, the OMPS NO₂ retrieval differences due to the profile differences can lead to a NMB of -7.5% (Fig S2), which is still smaller than the prior GEOS-Chem simulation NMB (10.9%, Fig. 3l). Second, a NMB of 10.9% for model NO₂ VCD simulation is not a very large value, as the difference between satellite NO₂ VCD retrievals and ground-based measurements could be comparable to this value. For example, Krotkov et al. (2017) shows that OMI NO₂ VCD retrievals, on average, are ~10% larger than ground-based FTIR spectrometer.
380 Thus, current research should mainly focus on the change of the spatial distribution (such as linear correlation coefficient) rather than bias of prior and posterior GEOS-Chem NO₂ VCD simulation. Finally, given that linear correlation coefficient between OMPS retrievals and that are modified through integration of averaging kernel and NO₂ vertical profile from this study is as large as 0.99, averaging kernel is not treated in the OMPS NO₂ observation operator. In general, the E-SO₂ and E-NO₂ posterior simulations show better results than E-joint,
385 which may be affected by the value of γ , which we will discuss in Sect. 4.3.

4.1.2 Emissions

The anthropogenic SO₂ and NO_x prior MIX emissions for October 2010 and posterior emissions from E-SO₂, E-NO₂, and E-joint for October 2013 are shown in Fig. 4. SO₂ and NO_x hot spots are found in the prior emissions over both the North China Plain and Eastern China, while large SO₂ emissions are also at Southwestern China.

390 Anthropogenic SO₂ emissions over China are 1166 Gg S in prior MIX for October 2010 (Fig. 4a), dropping 418 Gg S (Fig. 4b) and 306 Gg S (Fig. 4c), or 35.8% and 26.2%, in E-SO₂ and E-joint, respectively, for October 2013. The differences between the estimates of this study and the MIX emission inventory, however, should not be considered as trends, and they are derived from different approaches. Posterior E-joint total anthropogenic SO₂ emissions are 112 Gg, or 15% larger than E-SO₂ over China (Fig. 4e). Regionally, positive differences between

395 E-joint and E-SO₂ anthropogenic SO₂ emissions are over most areas of Central China and Eastern China, and relative difference is up to 100% over Shanxi province. (Fig. 4f). Grids with large differences are generally in locations where prior anthropogenic SO₂ emissions are larger, which means the pattern is affected by the fact the algorithm optimize emission scale factors rather than emissions directly. Anthropogenic NO_x emissions over China are reduced by 5.8% and 6.5% , from 714 Gg N in prior MIX for October 2010 (Fig 4g) to 672 Gg N (Fig.

400 4h) in E-NO₂ and 667 Gg N (Fig. 4i) in E-joint for October 2013. Although the relative difference between E-joint and E-NO₂ proved to be less than 2% in terms of total anthropogenic NO_x emissions over China (Fig. 4k), it is up to 40% over Shanxi province, and both grids with large positive differences and grids with large negative differences exist over North China Plain (Fig. 4 l).

4.1.3 Independent evaluation with OMI data

405 The optimized emission inventories are evaluated by comparing prior and posterior GEOS-Chem simulations of SO₂ and NO₂ with OMI VCDs as shown in Fig. 5. We only focus on regions covered by OMPS observations, although smaller changes of emissions exist in outskirts regions where OMPS observations are not used. High SO₂ levels are shown over the North China Plain and the Sichuan Basin in both the prior and posterior simulations while OMI only observes hot spots over the former region (Fig. 5a-d). When validating with OMI SO₂ VCDs, the

410 NMB is ~300% in the prior simulation, and it reduces to ~100% in E-SO₂ and ~130% in E-joint (Fig. 5i). Not only is the NMB reduced, but the spatial distributions are also improved with the NCRMSE reducing from ~1.6 in the prior simulation to ~0.7 in E-SO₂ and ~0.8 in E-joint, which is much closer to ~0.6 when comparing OMPS observations with OMI observations (Fig. 5i). For NO₂, OMI observations and the prior and posterior simulations show large NO₂ concentrations over the North China Plain and Eastern China (Fig. 5e-h). The improvements for

415 E-NO₂ and E-joint are reflected in terms of R when evaluating with OMI tropospheric VCDs, although the two
experiments show larger negative NMB than the prior simulation (Fig. 5j). In all the evaluations, OMI SO₂ and
NO₂ VCD retrievals are not corrected by calculating new air mass factors that are derived from integrating
scattering weights and corresponding vertical profiles of GEOS-Chem simulations of this study. However, Fig.
S4 shows similar improvements if new air mass factors are applied, although statistic metric values are slightly
420 different.

Here, OMPS observations and GEOS-Chem simulations are compared with OMI observations as an evaluation
of posterior emission inventories, but it is not assumed that OMI provides the true status of SO₂ and NO₂ in the
atmosphere. OMI and OMPS observe the same trend direction of SO₂ (NO₂) over China, but the strengths of trend
425 are quite different (Wang and Wang, 2020). OMPS SO₂ average is ~0.14 DU, or ~95% larger than OMI SO₂, and
the R of the two products is 0.81 (Fig. 6b). Thus, it is reasonable that posterior SO₂ is larger than OMI observations
by ~100% in E-SO₂ and ~130% in E-joint. OMPS NO₂ is ~24% smaller than OMI (Fig. 6d), which explains why
the posterior NO₂ simulations have larger negative NMB than the prior simulation when compared with the OMI
observations. Our analysis also shows that the systematic difference among various satellite products for the same
430 species (such as SO₂ or NO₂) can lead to biases in constraining emissions, but the posterior GEOS-Chem
simulations still show in terms of the spatial distribution of SO₂ and NO₂.

4.2 The impacts of QC and spatial balance

The results of E-SO₂-noQC-noBL and E-SO₂-noBL are compared with E-SO₂ to show the impacts of QC and
spatial balance. Both OMPS retrievals and the GEOS-Chem prior simulations show that SO₂ VCDs over Inner
435 Mongolia and the Sichuan Basin (grid cells M and S, respectively in Fig. 7) are smaller than those over the North
China Plain; this pattern reverses in the posterior E-SO₂-noQC-noBL simulation where SO₂ over the North China
Plain becomes smaller than that over grid cells M and S. Grid cell M becomes more reasonable after conducting
the data quality control by removing OMPS SO₂ in any grid cells where prior GEOS-Chem SO₂ VCDs are less
than 0.1 DU (e.g., as in E-SO₂-noBL, as shown in Fig. 7d). QC helps to improve models over grid cell M, as the
440 data removed are close to Inner Mongolia, and are generally less than 0.1 DU, which are comparable to the
retrieval error. SO₂ over grid cell S from E-SO₂-noBL (Fig. 7d) is, however, still larger than that over the North
China Plain, compared with the better spatial pattern from E-SO₂ (Fig. 3c). Thus, QC and spatial balancing of the
cost function together improve the spatial pattern of the posterior GEOS-Chem SO₂ VCD simulation.

4.3 The impacts of γ on joint assimilations

445 In addition to setting γ as 200 in E-joint, we test the impacts of using various γ values on joint assimilation in E-
joint-d γ for October 2013. All the SO₂ and NO₂ VCDs from prior and posterior E-joint and E-joint-d γ simulations
are compared with OMPS counterparts (Fig. 8a-b). Regardless of the γ values used, all the posterior simulations
of SO₂ show smaller NMB and NCRMSE than the prior simulation when validating against OMPS and OMI
450 counterparts, but the extents of improvement vary. When γ is 20, 50, or 100, the SO₂ terms are obviously under-
constrained, and GEOS-Chem SO₂ NCRMSE, evaluated with OMPS observations, changes from ~1.8 in the prior
simulation to in the range of ~1.4 to ~1.7 in the posterior E-joint-d γ simulations, which are much larger than ~0.7
in E-SO₂ (Fig. 8a). Similarly, when γ is no larger than 100, the bias of GEOS-Chem SO₂, validated with OMPS
observations, only reduces from ~100% to ~75%, compared to ~25% in E-SO₂ (Fig. 8a), and the posterior SO₂
emissions are in the range of 1055 Gg S to 1143 Gg S, which are much larger than 748 Gg S from E-SO₂ (Table
455 3). When γ is in the range of 200 to 2000, the SO₂ simulation results and emissions from joint assimilations are
more similar to that from E-SO₂ than that with γ no larger than 100 (Fig. 8a and Table 3). Similar to SO₂, the
GEOS-Chem simulations of NO₂ in the sensitivity experiments improve in terms of R and NCRMSE in all joint
assimilation tests, but the significance of γ is less than that for SO₂. NO₂ NCRMSE is ~0.4 in the prior simulation
when evaluating with OMPS counterparts, compared to the range of ~0.2 to ~0.25 in E-joint, E-joint-d γ and E-
460 NO₂ (Fig. 8b). The posterior NO_x emissions are in the range of 662 Gg N to 682 Gg N, compared with 672 Gg N
in E-NO₂ (Table 3).

The impacts of γ are also reflected when evaluating SO₂ and NO₂ simulations with OMI retrievals (Fig. 8c-d).
Small γ values of 20, 50, and 100 lead to a much larger bias and NCRMES for SO₂ from E-joint-d γ than that from
465 E-SO₂. For NO₂, these small γ values make results from E-joint-d γ very similar to that from E-NO₂.

Considering all of the above analyses, the results with γ in the range of 200 to 2000 are deemed acceptable. The
E-joint-d γ ($200 \leq \gamma \leq 2000$) emissions are within -3% to 15% of E-SO₂ for SO₂ and $\pm 2\%$ of E-NO₂ for NO_x in
terms of total anthropogenic SO₂ and NO_x emissions over China. When evaluating with OMPS observations, the
470 NCRMSE of using the posterior emissions from the separate and joint ($200 \leq \gamma \leq 2000$) inversions are ~60% and
~45%-60% smaller than that of using the prior emissions for SO₂, respectively, and ~50% and ~38%-50% smaller
than that of using the prior emissions for NO₂, respectively.

When evaluating with OMI retrievals, joint inversion shows better results than separate inversion for SO₂ or NO₂,
475 but not both, depending on the value of γ . When γ is 20, 50, or 100, NO₂ NCRSME for E-joint-d γ improvement
appears to be smaller than that for E-NO₂, but SO₂ NCRSME for E-joint-d γ is larger than that for E-SO₂.
Conversely, when γ is 1000, 1500, or 2000, SO₂ NCRSME for E-joint-d γ is smaller than that for E-SO₂, but NO₂
NCRSME for E-joint-d γ is larger than that for E-NO₂. This is similar to the findings by Qu et al., (2019b) in which
the months when joint inversion shows better result than separate inversion for SO₂ (NO₂) have worse result for
480 NO₂ (SO₂). The benefit of joint inversion for improving only one species is similar to Qu et al. (2019b) and is
likely due to the complicated relationship between these two species through different chemical pathways. For
example, O₃ and OH are key species that connect the chemistry of SO₂ and NO₂ and aerosols can affect the
photolysis and heterogenous chemistry. Hence, while joint inversion to improve both species cannot be
demonstrated here, it should be reviewed as the first step of simultaneously assimilating multiple species
485 (including AOD, NH₃, and other trace gases) to optimize emissions. Until then, the system is not ready to
holistically evaluate the benefits of joint assimilation to improve the model in a systematic manner. It is worthy
noting that Xu et al. (2013) showed the feasibility of using MODIS cloud-free radiance to optimize emissions of
SO₂ and NO₂ at the same time. Future research should add the aerosol optical depth or visible reflectance (as well
as tropospheric O₃ if reliable) as constraints to further evaluate the benefits of joint assimilation for improving
490 model overall performance in a systematic matter.

4.4 The impacts of NH₃ emission

In the single-species inversions, NH₃ emission uncertainty has weaker impacts on posterior SO₂ emissions than
NO_x emissions. Posterior SO₂ emissions over China are 748 Gg S in the 100% NH₃ emission scenario (E-SO₂),
and they only slightly reduce to 747 Gg S and 745 Gg S when NH₃ emissions are 50% (E-SO₂-0.5NH₃) and 20%
495 (E-SO₂-0.2NH₃) of the original values, respectively (Table 4). The largest relative changes at model-grid-cell
scale are only -2.5% (Fig. 9a) for E-SO₂-0.5NH₃ for and -4.7% (Fig. 9b) for E-SO₂-0.2NH₃. All these results can
be explained by considering how changes of NH₃ can potentially impact the lifetimes of SO₂ and NO₂ and hence
affect SO₂ and NO₂ VCD simulations. When the NH₃ emissions decrease to 50%, and 20% SO₂ VCDs only
increase up to 3.8% and 6.1%, respectively, in some grid cells over the Sichuan Basin in the prior simulations,
500 and these changes are even much smaller over the North China Plain (Fig. 10a-b), as NH₃ has no direct effect on
the life cycle of SO₂. This is understandable because in GEOS-Chem, once SO₂ is oxidized to H₂SO₄, SO₄²⁻
remains as particulate sulfate regardless it is neutralized by NH₃ or not (Wang et al., 2008). Hence, the reductions

of NH₃ to 50% and 20% overall has minimal (negligible) impact on SO₂ amount in the prior simulation and the posterior separate SO₂ emission inversion.

505

Although the posterior NO_x emissions in the scenarios of 50% (E-NO₂-0.5NH₃) and 20% (E-NO₂-0.2NH₃) NH₃ emission experiments of the original values are 5 Gg N (0.7%) and 19 Gg N (2.8%), respectively, which are smaller than those when using the original (E-NO₂) NH₃ emissions over China (Table 4), the reduction is up to -4.0% (Fig. 9e) for E-NO₂-0.5NH₃ and -9.1% (Fig. 9f) for E-NO₂-0.2NH₃ in individual grid cells. These decreases are understood by simultaneous reduction of nitrate by 59.5% (Fig. 12h vs. 12g) and 80.5% (Fig 12i vs. 12g) and ammonium by 39.6% (Fig. 12n vs. 12m) and 67.5% (Fig. 12o vs. 12m), which leads to large reduction of the hydrated aerosol surface area for heterogeneous N₂O₅ chemistry at night, hence overall NO₂ lifetime (Fig. 10c-d). N₂O₅ normally forms at night by reaction between NO₂ and NO₃, and thermally decomposes back to NO₂ and NO₃ (Seinfeld and Pandis, 2016), and hence the amount of N₂O₅, NO₂, and NO₃ are in equilibrium through the reversible reaction. Since the hydrolysis of N₂O₅ to form HNO₃ mainly occurs on hydrated aerosol particles (Seinfeld and Pandis, 2016), the decrease of hydrated aerosol surface area (due to reduction of NH₃ emission) leads to less hydrolysis of N₂O₅ (an important sink for atmospheric NO_x) and subsequently more NO₂ to be in the equilibrium with N₂O₅ at night. As a result, the reduction of NH₃ emissions further increases the positive bias in the prior NO₂ simulations when comparing with OMPS observations, and to compensate such large positive bias, non-negligible decreases in the posterior NO_x emissions are required (Fig. 9 e and f). The reduction of nitrate and ammonium aerosols can also increase sunlight reaching troposphere, hence photolysis O₃ and NO₂. Figure S5 separates the impacts of increase of photolysis O₃ and NO₂ and decrease heterogeneous N₂O₅ chemistry on NO₂ lifetime and shows that the former is negligible compared with the latter.

525 The decreases of posterior SO₂ and NO_x emissions in the joint inversions caused by the reduction of NH₃ emissions are stronger than that in the separate inversions (Table 4 and Fig. 9). Although the changes of NH₃ emissions only have slight impacts on the SO₂ separate inversions (E-SO₂, E-SO₂-0.5NH₃, and E-SO₂-0.2NH₃), the posterior SO₂ emission is 802 Gg S in E-joint-d γ ($\gamma=500$), down to 783 Gg S (decreasing by 2.4%) and 746 Gg S (decreasing by 7.0%) in E-joint-0.5NH₃- $\gamma 500$ and E-joint-0.2NH₃- $\gamma 500$, respectively (Table 4); in some grid cells, the relative reductions are up to -9.0% (Fig. 9c) for E-joint-0.5NH₃- $\gamma 500$ and -27.7% (Fig. 9d) for E-joint-0.2NH₃- $\gamma 500$. For posterior NO_x emissions at the grid cells, the relative changes are up -15.2% (Fig. 9g) for E-joint-0.5NH₃- $\gamma 500$ and -29.4% (Fig. 9h) for E-joint-0.2NH₃- $\gamma 500$ with respect to E-joint-d γ ($\gamma=500$).

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4.5 Aerosol responses to emission changes

Although SO₂ emissions over the North China Plain (E-joint-d γ ($\gamma=500$)) have decreased by more than 50%, and
535 NO_x emissions have also been reduced, reductions of Sulfate-Nitrate-Ammonium (SNA) Aerosol Optical Depth
(AOD) over the same region are only up to 10% (Fig. 11). This is because the North China Plain is mainly polluted
by nitrate rather than sulfate (Fig. 12a-l), and the reduction of SO₂ emissions will increase nitrate loadings in the
atmosphere (Fig. 12g-l), which is also consistent with Kharol et al. (2013)'s research that shows nitrate
concentrations decrease as SO₂ emissions increase; the reduction of SO₂ emissions lead to less H₂SO₄ to react
540 with NH₃, which further favor the reaction of HNO₃ and NH₃ to form nitrate. As NH₃ emissions change reduce
by 50% and 80% ammonium column loadings decrease by ~40% and ~70% (Fig. 12g-l), respectively, and nitrate
column loadings decrease even by ~70% and ~90%, respectively (Fig. 12m-r).

5. Discussion and conclusions

We developed 4D-var observation operators for assimilating OMPS SO₂ and NO₂ VCDs to constrain SO₂ and
545 NO_x emissions through GEOS-Chem adjoint model. The approach is applied for case study over China for
October 2013 at 2°x2.5° resolution and the MIX 2010 is used as the prior emission inventory. Several experiments
of assimilating OMPS SO₂ and NO₂ separately and jointly are conducted, and SO₂ and NO₂ VCDs from the
GEOS-Chem prior and posterior simulations are compared with counterparts from OMPS and OMI.

550 OMPS SO₂ and NO₂ retrievals are separately and jointly used to constrain their corresponding emissions. In the
single-species inversions, posterior anthropogenic SO₂ and NO_x emissions are 748 Gg S and 672 Gg N for October
2013, down from 1166 Gg S and 714 Gg N in the prior MIX for October 2010, respectively. In the joint inversions
of assimilating OMPS SO₂ and NO₂ simultaneously, the cost function is balanced according to the values of
observational terms rather than the number of observations. When the cost function is well balanced (γ in the
555 range of 200 to 2000), the results of the joint inversions are within -3% to 15% of the single-species inversion for
total anthropogenic SO₂ emissions and $\pm 2\%$ for total anthropogenic NO_x emissions. However, the differences
between the separate and joint inversions are up to 100% and 40% in some model grid cells for anthropogenic
SO₂ and NO_x emissions, respectively. In comparison to OMPS observations, NCRMSE from joint inversions (γ
in the range of 200 to 2000) is reduced by ~45%~60% for SO₂ and ~38%~50% for NO₂, respectively, which is
560 close to the ~60% reduction from the SO₂ inversion and the ~50% reduction from the separate NO₂ inversion. To
obtain posterior emissions for both SO₂ and NO_x, the computational time for the joint inversion is only about ~50%

of the single-species inversions, when the latter are computed sequentially. Moreover, posterior GEOS-Chem SO₂ and NO₂ show improvements in terms of R when comparing against OMI observations, and the increase of posterior GEOS-Chem NO₂ negative NMB is ascribed to that the average of OMPS NO₂ over China is smaller than the OMI counterpart. Above all, the posterior emission increases the GEOS-Chem simulated spatial distributions of SO₂ and NO₂.

Both data quality control and spatially balancing the cost function play an important role for constraining SO₂ emissions. OMPS SO₂ retrievals over the regions where emissions are small are removed as VCDs are comparable to retrieval errors. A sensitivity study shows that if these data are included, it will lead to artifacts in the posterior SO₂ emission spatial distribution. Due to cloud screening, the number of OMPS SO₂ retrievals over the Sichuan Basin is much less than that over the North China Plain, which will lead to under-constraining over Sichuan Basin, if the observation error is assumed spatially constant. When the observation error is set based on the number of observations, the artifacts are avoided.

To investigate the impacts of the uncertainty of NH₃ emissions on posterior SO₂ and NO_x emissions, several inverse modeling experiments are conducted by setting prior NH₃ emissions to as 50% and 20% of their original values. The reduction of NH₃ emissions can lead to a larger decrease of posterior NO_x emissions and a smaller decrease of SO₂ emissions in separate assimilations, which ascribes to the NO₂ lifetime is more than the SO₂ affected by the change of NH₃ emissions. The impacts of NH₃ emissions uncertainty on both posterior SO₂ and NO_x emissions in joint assimilations are stronger than separate assimilations.

Large SO₂ emissions are mainly produced over the Sichuan basin and the North China Plain, while AOD responses to the changes of SO₂ emissions are quite different over the two regions. The reduction in SO₂ emissions can effectively decrease AOD over the Sichuan Basin, while AOD declines only slightly over the North China Plain, which can be ascribed to (1) nitrate rather than sulfate is dominant over the North China Plain and (2) the reduction of SO₂ emissions facilitate the formation of additional nitrate. AOD over the North China Plain is mainly determined by NO_x and NH₃ emissions rather than SO₂ emissions.

All emissions are constrained on the monthly scale and at the coarse spatial resolution of 2°×2.5° in this study, as OMPS observations are provided once per day at the resolutions as coarse as 50 × 50 km² at nadir and 50 × 190 km² at edge and the 4D-Var data assimilation at finer spatial resolution (on the order of 0.1 degree) would be

computationally prohibitive. The approach, however, has the potential for optimizing emissions at daily to weekly scale and in fine spatial resolution (on order of ~ 10 km) from future satellite observations at high spatial and temporal resolutions. In particular, TEMPO (monitoring North America), GEMS (monitoring East Asia), and Sentinel-4 (monitoring Europe) are to be launched in the next several years, and all of these satellites will provide hourly SO₂ and NO₂ observations during the daytime with resolution of 2.1×4.4 km², 7×8 km², 8.9×11.7 km², respectively. Furthermore, in Part II of this work, we develop various downscale methods to apply these coarser-resolution top-down estimates of emissions for air quality forecasts and evaluate the forecasts with surface measurements, both at the finer spatial scale (Wang et al., 2019).

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Table 1. Different experimental design for using OMPS SO₂ and NO₂ to constrain corresponding emissions over China for October 2013.

Name	Data	SO ₂ error ^b	NO ₂ error	γ^c	QC for SO ₂ ^d
E-SO ₂	SO ₂	0.2 DU x \sqrt{N}	NA	1	Yes
E-NO ₂	NO ₂	NA	0.011 DU	NA	NA
E-joint	SO ₂ and NO ₂	0.2 DU x \sqrt{N}	0.011 DU	200	Yes
E-SO ₂ -noQC-noBL	SO ₂	0.2 DU	NA	1	No
E-SO ₂ -noBL	SO ₂	0.2 DU	NA	1	Yes
E-joint-d γ	SO ₂ and NO ₂	0.2 DU x \sqrt{N}	0.011 DU	20 to 2000 ^e	Yes

^aSee description of these names in detail in Set. 3.2.

^b N in this column is number of OMPS overpass that have SO₂ observation in the 2x2.5 GEOS-Chem grid cell.

835 ^c γ is a parameter used to balance SO₂ and NO₂ observation terms in the cost function.

^dOMPS SO₂ retrievals in the 2x2.5 grid cell where the prior GEOS-Chem simulation is less than 0.1 DU are removed.

^eAll these γ values (20, 50, 100, 300, 500, 1000, 1500, and 2000) are used.

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Table 2. Different experimental design for assessing the impacts of NH₃ emission inventories on using OMPS SO₂ and NO₂ to constrain corresponding emissions over China for October 2013^a.

Name ^b	Data	γ^c	NH ₃ emissions
E-SO ₂ -0.5NH ₃	SO ₂	NA	50%
E-NO ₂ -0.5NH ₃	NO ₂	NA	50%
E-joint-0.5NH ₃ - γ 500	SO ₂ and NO ₂	500	50%
E-SO ₂ -0.2NH ₃	SO ₂	NA	20%
E-NO ₂ -0.2NH ₃	NO ₂	NA	20%
E-joint-0.2NH ₃ - γ 500	SO ₂ and NO ₂	500	20%

^aData quality control and observation errors are same as E-joint in Table 1.

^bSee description of these names in detail in Set. 3.2.

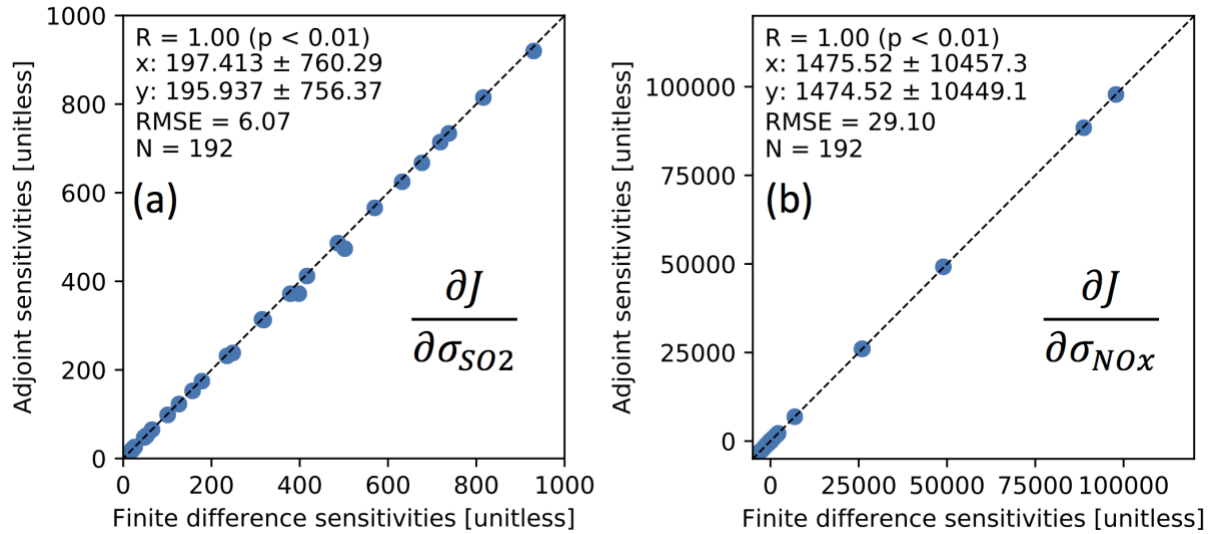
845 ^c γ is a parameter used to balance SO₂ and NO₂ observation terms in the cost function.

Table 3. Posterior anthropogenic emissions for October 2013 from E-joint, E-joint-d γ , E-SO₂ and E-NO₂.

Experiment name or γ	20	50	100	200	300	500	1000	1500	2000	E-SO ₂ or E-NO ₂
SO ₂ [Gg S]	1143	1110	1055	860	795	802	733	730	728	748
NO _x [Gg N]	681	682	682	667	662	664	668	666	674	672

Table 4. Posterior anthropogenic emissions for October 2013 under different NH₃ emission scenarios

Name	SO ₂ emissions [Gg S]	NO _x emission [Gg N]
E-SO ₂	748	NA
E-SO ₂ -0.5NH ₃	747	NA
E-SO ₂ -0.2NH ₃	745	NA
E-NO ₂	NA	672
E-NO ₂ -0.5NH ₃	NA	667
E-NO ₂ -0.2NH ₃	NA	653
E-joint-d γ ($\gamma=500$)	802	664
E-joint-0.5NH ₃ - $\gamma 500$	783	646
E-joint-0.2NH ₃ - $\gamma 500$	746	629



855 **Figure 1. Validation of adjoint model sensitivity through comparison to centered finite difference results for a 3-day simulation. Shown here are the sensitivity of column cost function (penalty term is not included, and horizontal transport is turned off) with respect to logarithm of anthropogenic SO₂ (a) and NO_x (b) emission scale factors: the 1:1 line (dotted), the number of grid columns (N), Root Mean Squared Error (RMSE), and correlation coefficient (R), and Means and standard deviations of finite difference sensitivity and adjoint sensitivity (x and y).**

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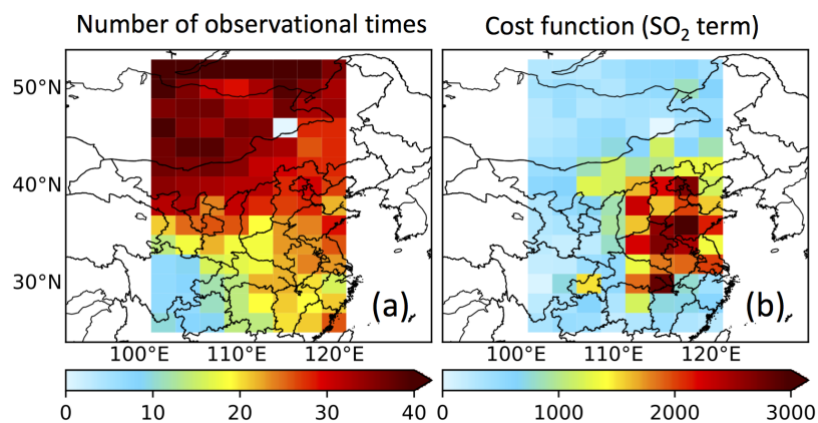
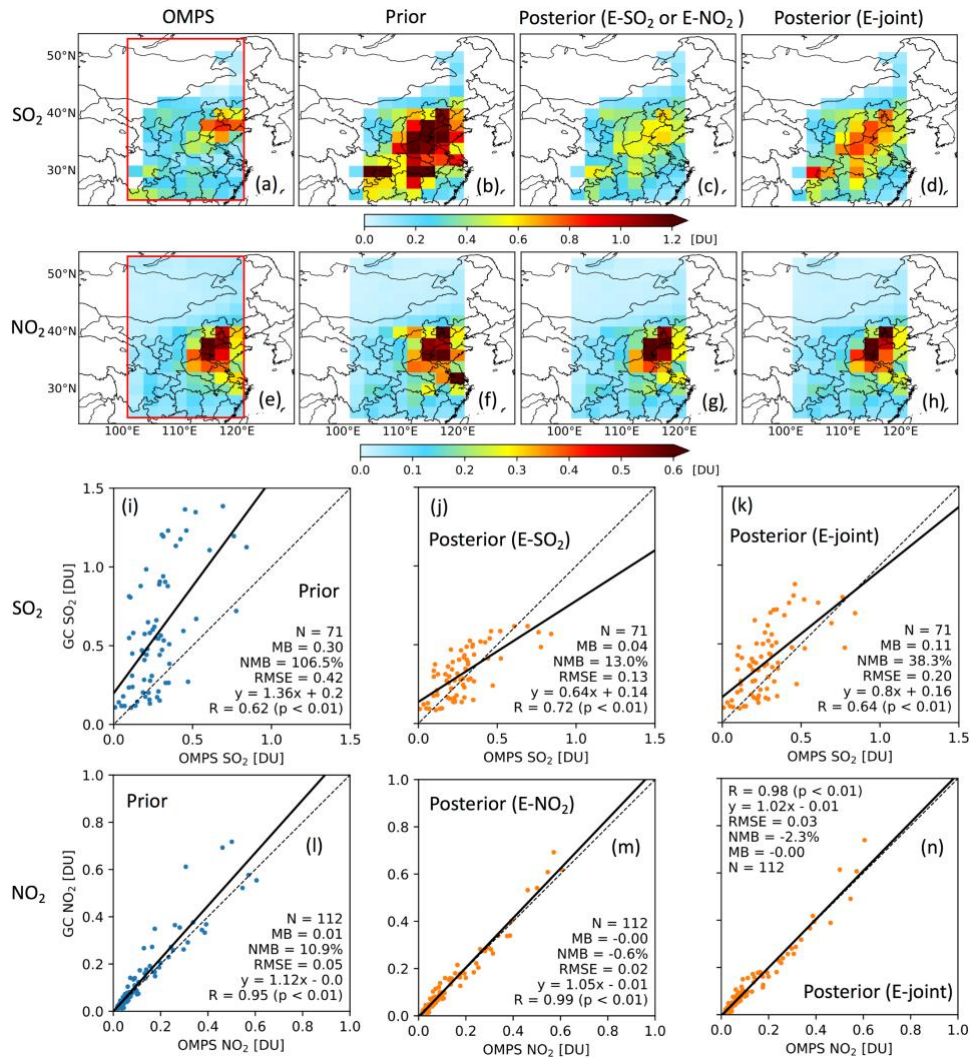


Figure 2. (a) and (b) are the numbers of the OMPS overpass time that provides SO₂ VCD retrievals and SO₂ term in cost function at first iteration, respectively, in October 2013

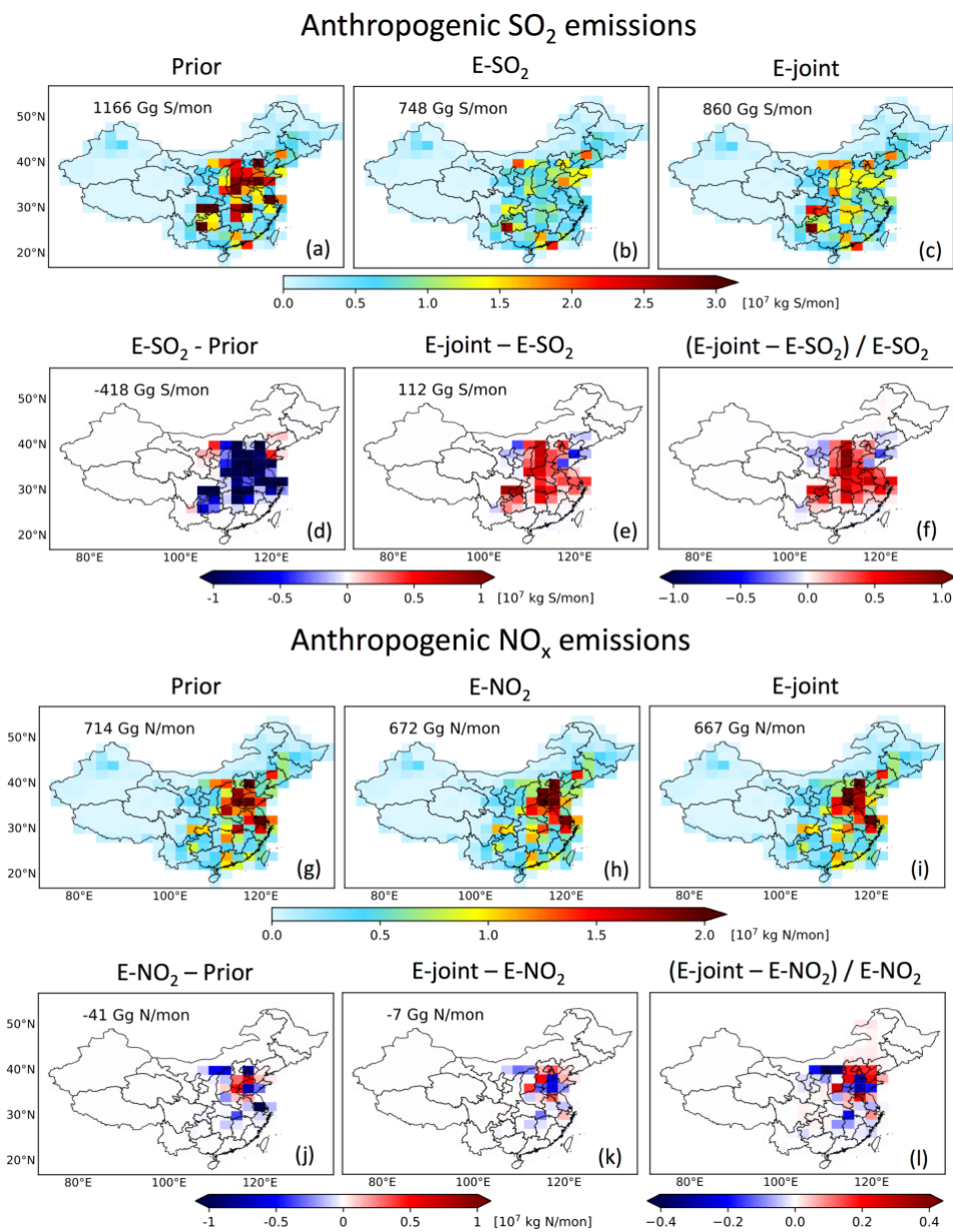


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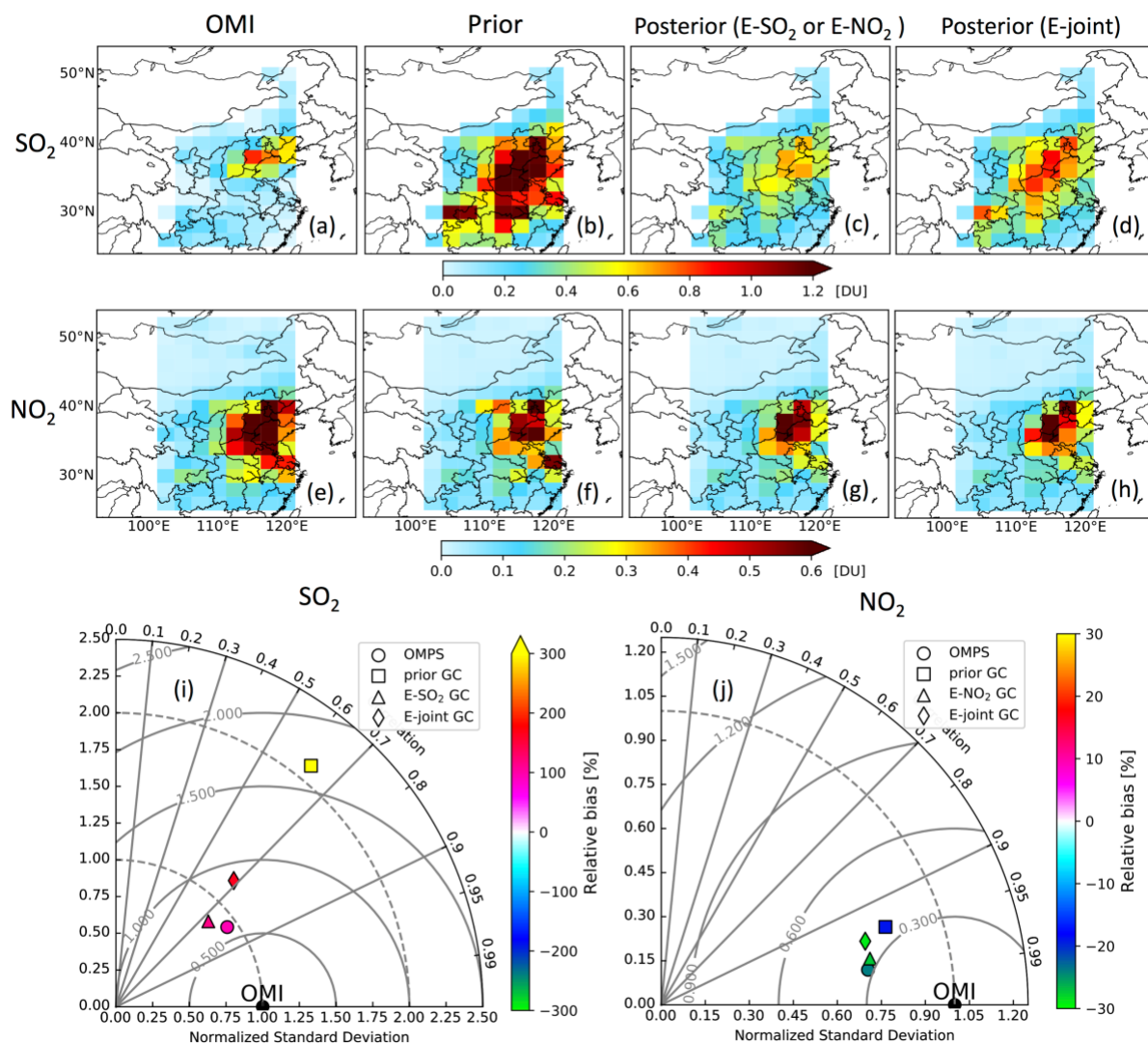
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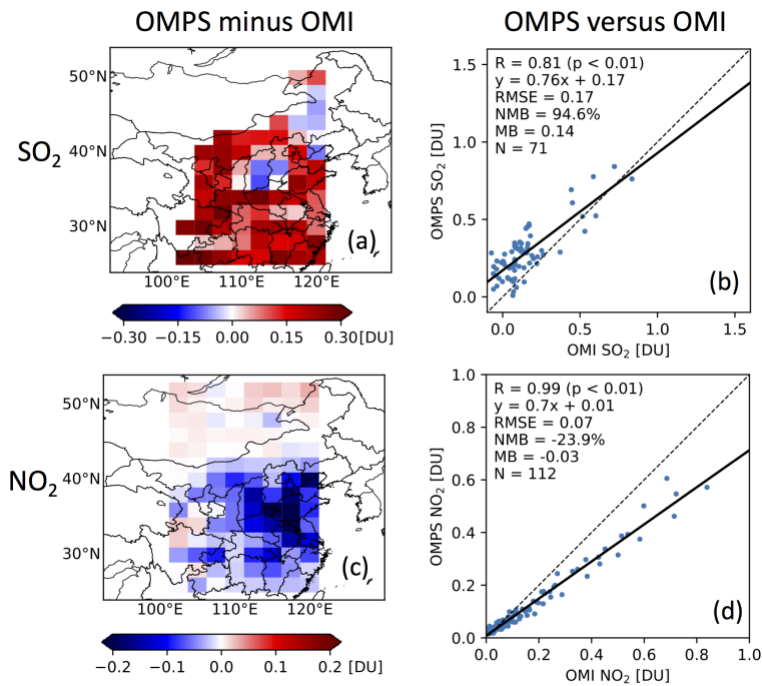
Figure 3. Comparisons of VCDs of SO₂ and NO₂ from the OMPS and the GEOS-Chem prior and posterior simulations in October 2013 over China. The first row is SO₂ VCDs from the OMPS (a), the prior simulation (b), the E-SO₂ posterior simulation (c), and the E-joint posterior simulation (d). The second row is NO₂ tropospheric VCDs from the OMPS (e), the prior simulation (f), the E-NO₂ posterior simulation (g), and the E-joint posterior simulation (h). The third row is the SO₂ VCD scatter plots of the GEOS-Chem prior (i), the E-SO₂ posterior (j), and the E-joint posterior (k) versus the OMPS, respectively. The last row is the NO₂ tropospheric VCD scatter plots of the GEOS-Chem prior (l), the E-NO₂ posterior (m), and the E-joint posterior (n) versus the OMPS, respectively. Linear correlation coefficient (R), linear regression equation, root mean squared error (RMSE), normalized mean bias (NMB), mean bias (MB), and number of observations (N) are shown over scatter plots.



880 **Figure 4.** The top is anthropogenic SO₂ emissions from prior MIX 2010 (a), posterior E-SO₂ (b), posterior E-joint (c), the difference between posterior E-SO₂ and prior MIX 2010 (d), the difference between posterior E-joint and posterior E-SO₂ (e), and the relative difference between posterior E-joint and posterior E-SO₂ (f) for October 2013. The bottom is similar to the top except that (1) it is for NO_x and (2) E-SO₂ is replaced by E-NO₂.



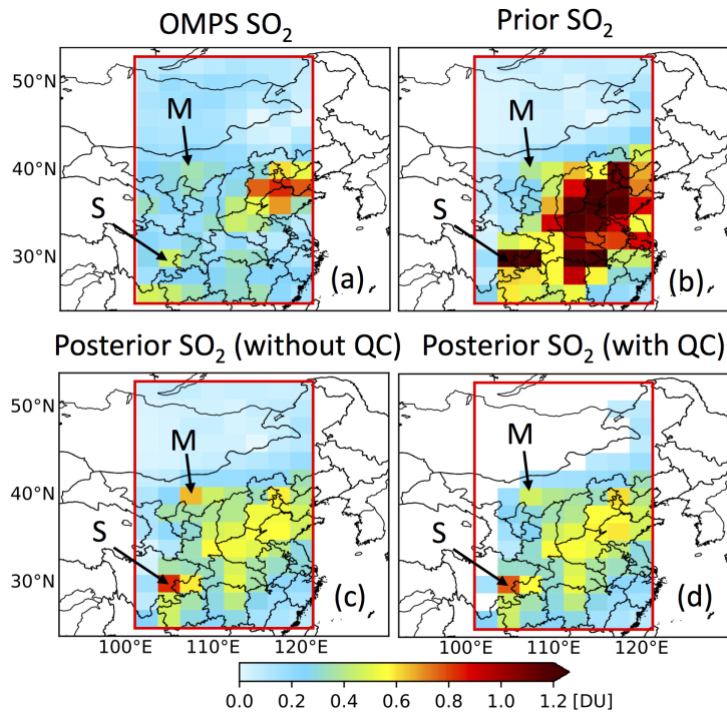
885 Figure 5. Comparisons of VCDs of SO₂ and NO₂ from the OMPS and the GEOS-Chem prior and posterior simulations
 with that from the OMI in October 2013 over China. The first row is SO₂ VCDs from the OMI (a), the prior simulation
 (b), the E-SO₂ posterior simulation (c), and the E-joint posterior simulation (d). The second row is NO₂ tropospheric
 VCDs from the OMI (e), the prior simulation (f), the E-NO₂ posterior simulation (g), and the E-joint posterior
 890 simulation (h). The third row is Taylor diagrams for comparing GEOS-Chem simulations (squares for prior, triangles
 for posterior E-SO₂ or E-NO₂, and diamonds for E-joint) and OMPS observations (circles) with OMI SO₂ (i) and NO₂
 (j).



895 Figure 6. (a) and (b) are the difference between OMPS and OMI SO₂ and scatter plot of OMPS versus OMI SO₂. (c) and (d) are similar (a) and (b), but for NO₂. Linear correlation coefficient (R), linear regression equation, root mean squared error (RMSE), normalized mean bias (NMB), mean bias (MB), and number of observations (N) are shown over scatter plots.

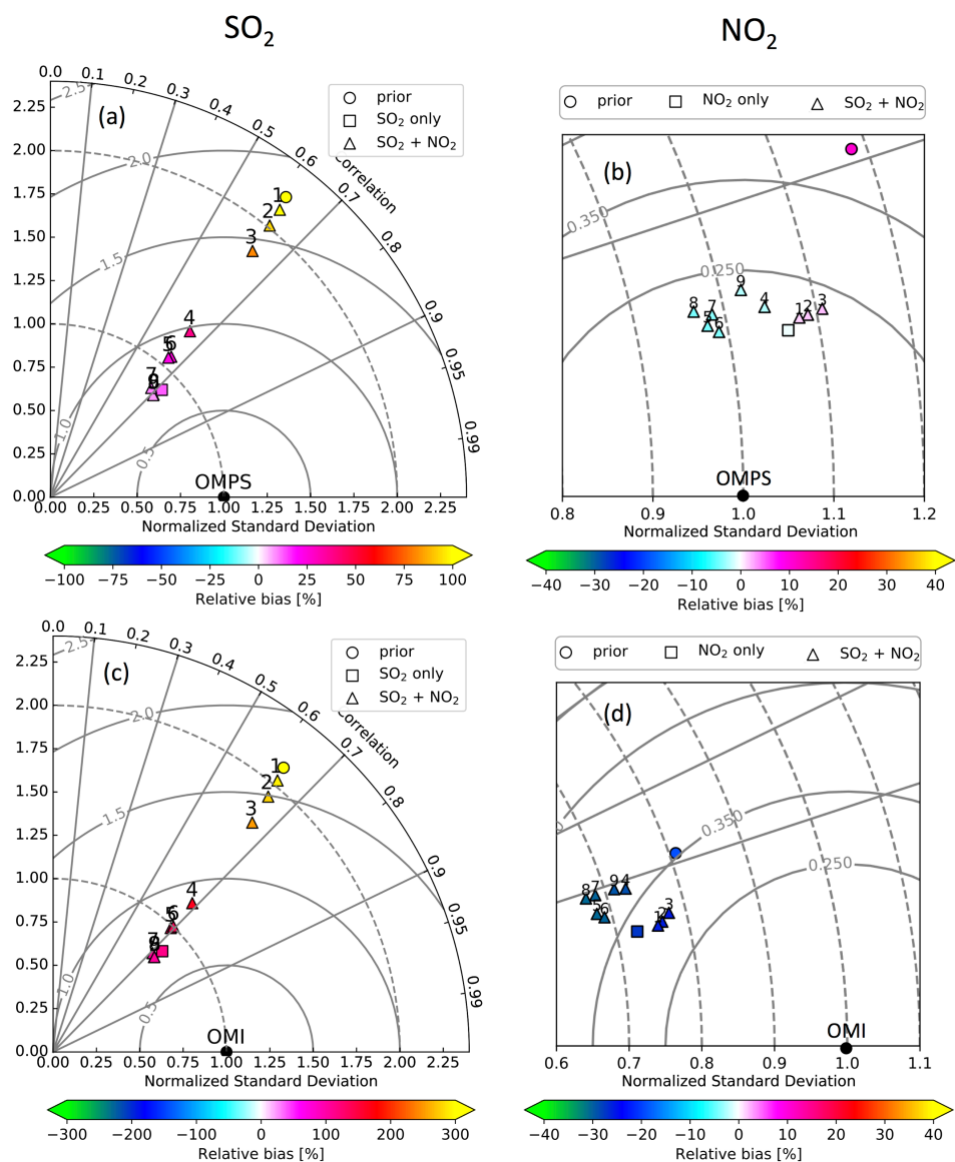
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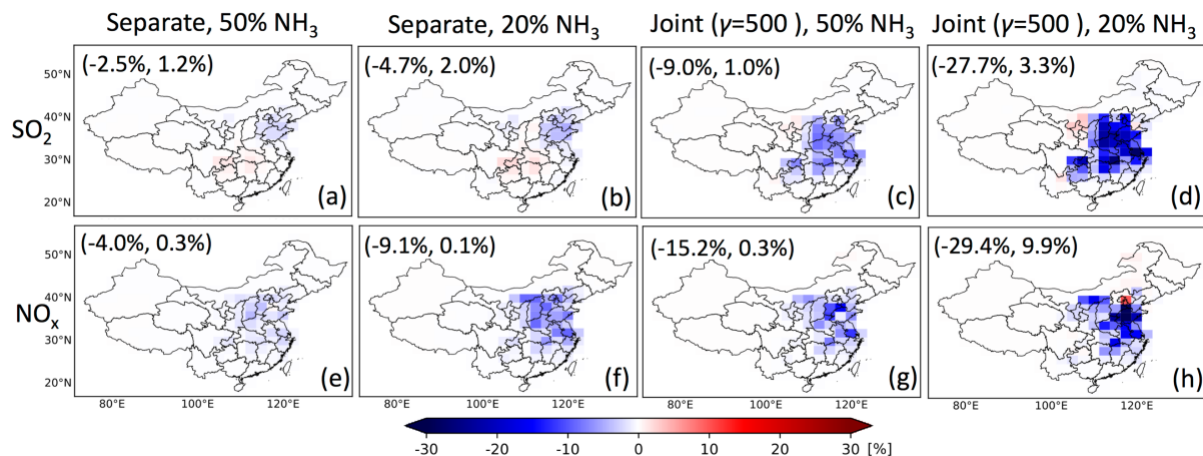


910 **Figure 7. SO₂ VCD in October 2013 from OMPS (a), prior GEOS-Chem simulation (b), posterior GEOS-chem simulation through using all OMPS data in the red box (c), and posterior GEOS-chem simulation through using only OMPS data that are in the grid cell where GEOS-Chem prior simulation of VCD is larger than 0.1 DU. For posterior simulation, we only plot SO₂ VCD over grid cells where OMPS data are used to constrain emissions. M and S point to a grid cell in Inner Mongolia and Sichuan basin, respectively.**

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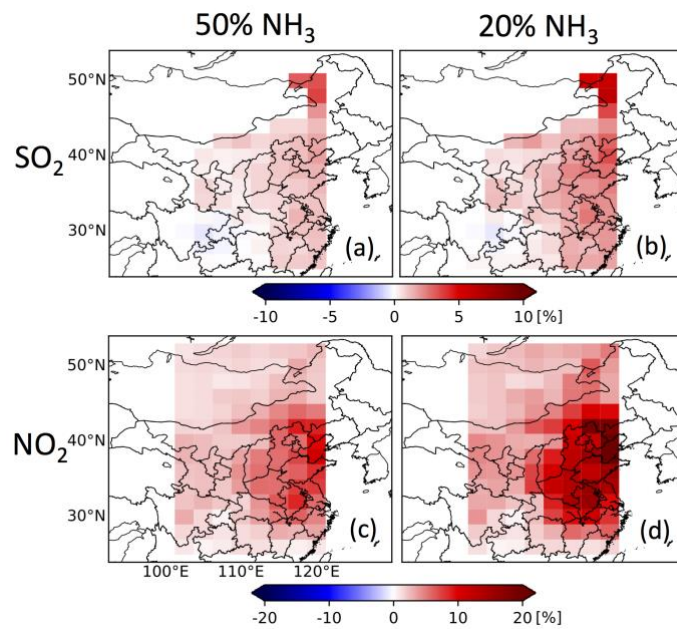
920 **Figure 8.** Taylor diagram of comparing GEOS-Chem simulation with OMPS (a for SO₂ and b for NO₂) or OMI (c for SO₂ and d for NO₂) in October 2013. Circles, squares, and triangles represent GEOS-Chem simulations using prior MIX 2010 emissions, posterior emissions constrained by single species (E_SO2 for a and c, E_NO2 for b and d), and posterior emissions constrained through joint inversion (E_joint), respectively. Different triangles labeled by numbers represent different γ values in Eq. (1), and 1 through 9 correspond to 20, 50, 100, 200, 300, 500, 1000, 1500, and 2000, respectively.



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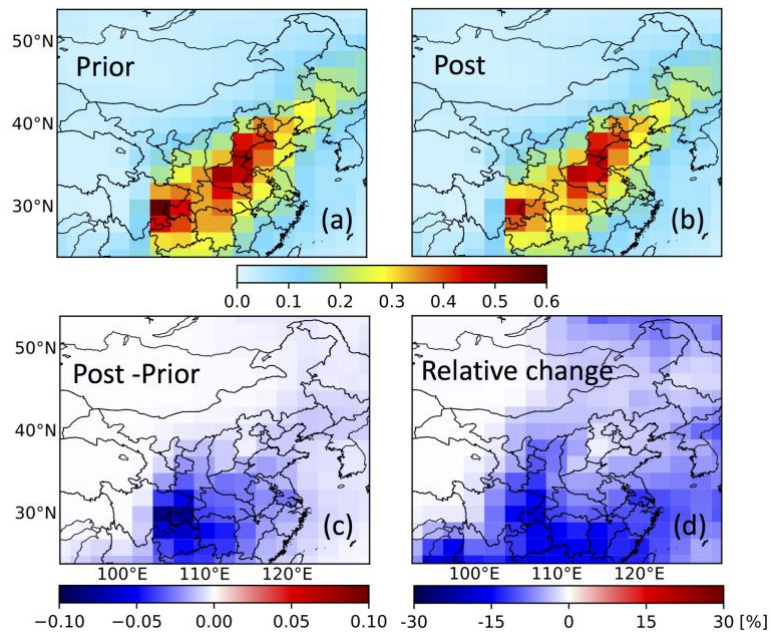
Figure 9. Relative changes of posterior SO₂ (top row) and NO_x (bottom row) emissions from the scenarios of perturbing NH₃ emissions with respect to that using original NH₃ emission inventory. (a) and (b) are relative changes of posterior SO₂ emissions from E-SO₂-0.5NH₃ and E-SO₂-0.2NH₃ with respect to that from E-SO₂, respectively. (c) and (d) are relative changes of posterior SO₂ emissions from E-joint-0.5NH₃- γ 500 and E-joint-0.2NH₃- γ 500 with respect to that from E-joint- γ ($\gamma=500$), respectively. (e) and (f) are relative changes of posterior NO_x emissions from E-NO₂-0.5NH₃ and E-NO₂-0.2NH₃ with respect to that from E-NO₂, respectively. (g) and (h) are similar to (c) and (d), respectively, but for posterior NO_x emissions. Minimum and maximum are shown in brackets.

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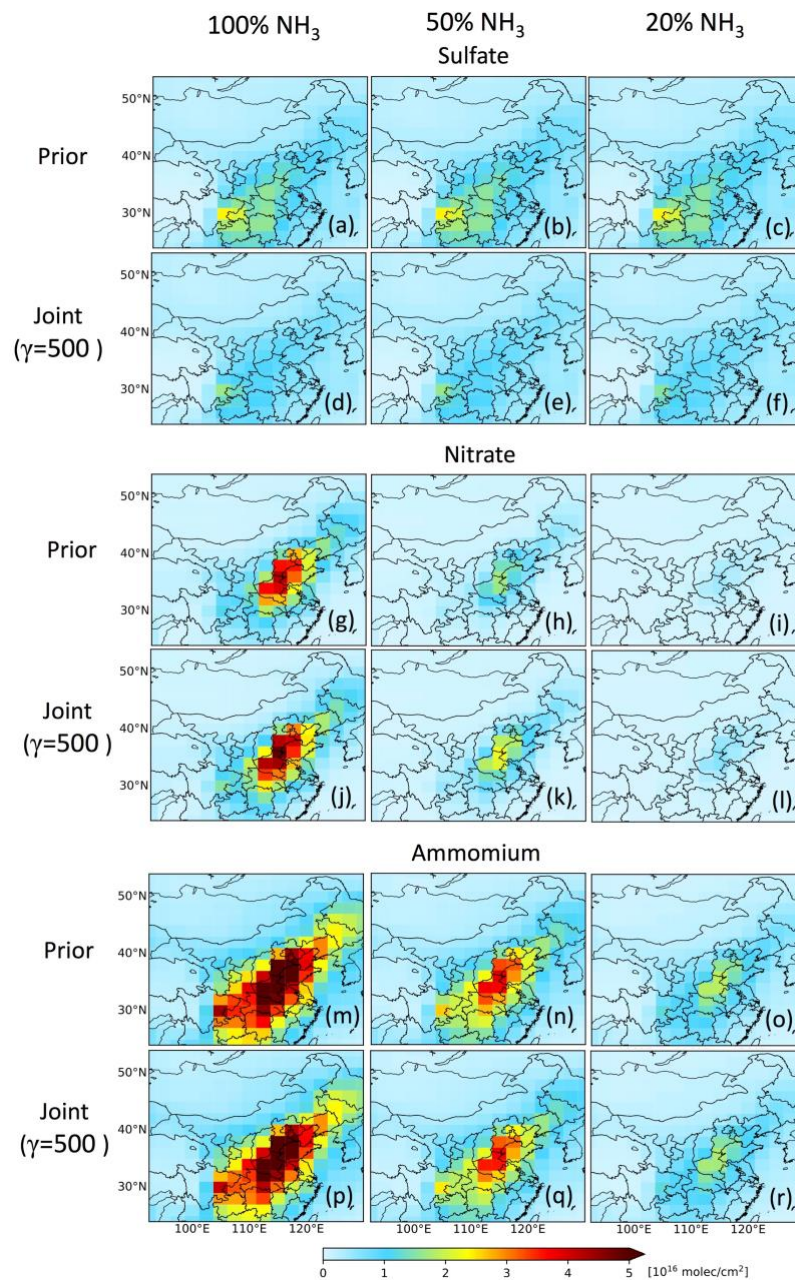
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Figure 10. Relative change of GEOS-Chem SO₂ VCDs when NH₃ emissions reduce to 50% (a) and 20% (b), respectively at OMPS overpassing time. (c) and (d) are similar to (a) and (b), respectively, but for NO₂.



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Figure 11. Sulfate-nitrate-ammonium aerosol optical depth in prior (a) and posterior joint inversion ($\gamma=500$) (b). (c) is the difference between (b) and (a), and (d) is relative change in percentage.



945 **Figure 12.** Sulfate, nitrate, and ammonium column loadings in different scenarios. (a), (b), and (c) are prior sulfate at 100%, 50%, and 20% NH₃ emissions, respectively. (d), (e), and (f) are posterior sulfate from joint inversions ($\gamma=500$) at 100%, 50%, and 20% NH₃ emissions, respectively. (g)-(i) and (m)-(r) are similar to (a)-(f), but for nitrate and ammonium, respectively.