We thank the two reviewers for the detailed and thoughtful review of our manuscript entitled "Development and application of observable response indicators for design of an effective ozone and fine particle pollution control strategy in China". Incorporation of the reviewers' suggestion has led to a much improved manuscript. Detailed below is our response to the issues raised by the reviewers. We also detail the specific changes incorporated in the revised manuscript in response to the reviewers' comments.

Reviewer #1:

[Comment]: *Identifying strategies that reduce the concentrations of secondary or mixed air pollutants most effectively is always a challenging work. This study partially answers this question by providing a new technique with combination of observation and RSM modeling indicators. Overall the paper is well written, I have minor comments for the authors to improve the paper and meet ACP requirements.*

[Response]: We thank the reviewer for recognition of the implications of the results of the analysis presented, and overall positive comments. We have followed all the comments and revised manuscript accordingly.

[Comment]: *The indicators are based on the chemical mechanisms and emissions in current models. Thus, the indicators may change for a different location or with improved mechanisms. I suggest authors add the limitations of this study in inclusion parts.*

[Response]: We agree with the reviewer that the indicators developed in this study were mainly based on the chemical mechanisms and emissions used in current study. They might change along with the improvement of scientific knowledge of chemical mechanisms. As the reviewer suggested, we point out such limitations in the revised manuscript, as follows.

(Page 22, Line 491-495) "We note that the discrepency between the observable indicator and the responsive indicator might also be influcenced by uncertainties in the chemical mechanism of CMAQ as well as prediction errors of the pf-RSM. The new indicators were designed based on the existing chemical mechanism, and the transition values might be refined in the future as our understanding of atmospheric chemical processes improves."

[Comment]: *Only the title uses "particle" to represent particulate matter.*

[Response]: We thank the reviewer for noticing this issue. To address such problem and to be consistent through the text, we have modified the "fine particular matter" into "fine particle" when defining the $PM_{2.5}$ in the abstract and the introduction section, as follows.

(Page 1, Line 19-21) "Therefore, this study developed new observable RSM-based indicators and applied them to ambient fine particle ($PM_{2.5}$) and ozone (O_3) pollution control in China."

(Page 3, Line 46-47) "In particular, ambient fine particles ($PM_{2.5}$) and ozone (O_3) are among the top risk factors for global mortality…"

[Comment]: *Clarifying some places and correcting grammar errors would help readers understand the paper better.*

[Response]: Followed the reviewer's suggestion, we corrected the grammar errors and did additional clarification in the revised manuscript.

[Comment]: *Lines 57-58, this sentence is not correct, for example, O3 and NOx are correlated, but it is not due to the similarities in their atmospheric processes.*

[Response]: We agree with the reviewer that the original statement is a bit misleading. We have clarified it in the revised manuscript as follows.

(Page 3, Line 57-59) "Chemical species in the atmosphere are often highly correlated with one another, since their concentrations are affected by common atmospheric physical processes (e.g., mixing and transport) and chemical reactions."

[Comment]: *Line 58, not proper to call PM2.5 as secondary pollutants.*

[Response]: We agree with the reviewer that the PM2.5 can also come from primary emissions. To make the statement more accurate, we have deleted the secondary in the revised manuscript as follows.

(Page 3, Line 59-61) "Concentrations of pollutants such as O_3 and $PM_{2.5}$ are typically determined based on the ambient levels of their gaseous precursors, implying that O_3 and $PM_{2.5}$ chemistry can be identified through a combination of concentrations of some of their related chemical species (i.e., indicators)."

[Comment]: *Lines 106-108, this sentence does not belong here.*

[Response]: We agree with the reviewer that the original location of this sentence is inappropriate. We have moved it to the beginning of that paragraph in the revised manuscript, as follows.

(Page 5, Line 104-105) "The design of an effective O_3 and $PM_{2.5}$ control strategy requires efficient quantification of air pollutant sensitivity to precursor emissions."

Reviewer #2:

[Comment]: *The manuscript by Xing et al. on development and application of observable response indicators uses response surface modeling to identify parameters that define key O3 and PM2.5 production regimes, and then correlates these with observable indicators, i.e. ratios of gas and aerosol phase concentrations that are routinely measured. This provides valuable information that could be used to help design effective air quality policy to simultaneously reduce levels of both O3 and PM2.5 which, as the authors point out, has been a*

challenge in China. The work is thus very relevant and suitable in scope for ACP. The paper is also very clearly written for the most part.

[Response]: We thank the reviewer for recognition of the implications of the results of the analysis presented, and overall positive comments.

[Comment]: *My main comments are summarized as follows. The study currently neglect any errors in the polynomial approximations of the full CTM at later stages in the analysis, which I think is an oversight.*

[Response]: We agree with the reviewer on the importance of considering the error of polynomial approximations of the CTM. In the development of pf-RSM, we have examined the performance of pf-RSM to ensure its accuracy to meet the criteria of a mean normalized error within 2% and a maximal normalized error within 10%. The large errors are mostly located in the marginal areas where the emissions were reduced to nearly zero and the concentrations will be very small. Thus, the errors in the pf-RSM predictions have limited influence on the shape of nonlinear curve of the response function. To address the reviewer's concern, we have added following description about the error of pf-RSM in the revised manuscript.

(Page 8, Line 164-171) "The pf-RSM performance in predicting $PM_{2.5}$ and O_3 responses has been evaluated in detail using leave-one-out cross validation as well as the out-of-sample validation method, with normalized errors all within 5% for both $PM_{2.5}$ and O_3 across the domain. Relatively large biases occurred for marginal cases, where emissions are controlled by nearly 100% and predicted concentrations are very small. These cases have limited influence on the shape of nonlinear curve of the response function. However, the RSM is developed from a suite of CMAQ simulations, and so uncertainties in the chemical mechanism used in CMAQ might influence the O_3 and $PM_{2.5}$ predictions."

[Comment]: *Further, it is not mentioned explicitly that responses being analyzed here are with respect to domain wide emissions perturbations (I suspect, as it isn't explained clearly). This limits the applicability of these responses for evaluation of regional air quality control strategies, as there would be errors in using these relationships to estimate a response to a regional change in emissions.*

[Response]: We agree with the reviewer that the response of PM2.5 and O3 to different regional sources varies significantly. As suggested in our previous study (Xing et al., 2011), the local NOx controls can be either beneficial or unbeneficial in reducing O3, while regional NOx controls usually exhibit benefits in reducing O3. The overall effects are determined by the combination of the selected local/regional control ratios. In this study, the same level of emission perturbations was applied across the country. That is because controls are more likely taken in multiple regions of China rather than only on one single region. In addition, the same level of local and regional reduction is suggested to achieve aggressive air quality goals as demonstrated in our previous study (Xing et al., 2019).

To clarify this point, we have provided additional discussion in the revised manuscript, as follows.

(Page 7, Line 156-161) "Though the responses of O_3 and $PM_{2.5}$ to local or regional emissions vary significantly as suggested in our previous study (Xing et al., 2011), we applied the same change ratio of each pollutant emission to all regions across China. This approach is consistent with the implementation of a multi-regional joint control

strategy, which is reasonable for China. The same level of local and regional emission reduction has been recommended to achieve China's aggressive air quality goals (Xing et al., 2019)."

Reference:

Xing, J., Wang, S. X., Jang, C., Zhu, Y., and Hao, J. M.: Nonlinear response of ozone to precursor emission changes in China: a modeling study using response surface methodology, Atmospheric Chemistry and Physics, 11, 5027-5044, 10.5194/acp-11-5027-2011, 2011.

Xing, J., Zhang, F., Zhou, Y., Wang, S., Ding, D., Jang, C., Zhu, Y. and Hao, J.: Least-cost control strategy optimization for air quality attainment of Beijing–Tianjin–Hebei region in China. Journal of environmental management, 245, 95-104, 2019.

[Comment]: *Lastly, here are a few definitions / concepts that would be useful for the authors to define upfront (definitions of indicators that general audiences may not be familiar with).*

[Response]: As the reviewer suggested, we have defined the indicators including DSN, GR, and AdjGR, and provided references for PR and FR in the revised manuscript.

[Comment]: *Overall, the methods and results are interesting and have merit; all of these issues could be addressed with revisions to the text and some additional work on error analysis.*

[Response]: We have followed the reviewer's suggestion and made modification correspondingly in the text. Hope the revised manuscript can meet the high standard for ACP journal.

[Comment]: *69: Please define DSN, GR, and AdjGR. Eventually I see later (line 233) that these are defined in the SI, but it would be more useful if they were defined earlier, or at least reference to where their definition can be found provided earlier.*

[Response]: As the reviewer suggested, we provide the definition of three indicators at the first time in the text, as follows.

(Page 4 Line 72-75) "Regarding $PM_{2.5}$ chemistry (more specifically for inorganic $PM_{2.5}$ sensitivities to NH_3 and NO_x), indicators such as the degree of sulfate neutralization (DSN), gas ratio (GR), and adjusted gas ratio (AdjGR) have been developed (defined in Text S1) to identify NH_3-poor or -rich conditions (Ansari and Pandis, 1998; Takahama et al., 2004; Pinder et al., 2008; Dennis et al., 2008)."

[Comment]: *71: Clarify that by "these" you are referring to indicators for O3. I don't believe this has been done for the SIA indicators such as AdjGR since total nitrate isn't routinely observable from space.*

[Response]: We agree with the reviewer that "these" is referring to O_3 indicator. As the reviewer suggested, we have clarified it in the revised manuscript and moved this sentence ahead of the PM chemistry indicator, as follows.

(Page 4 Line 68-72) "The O_3 indicators can be derived from surface-monitoring observations (Peng et al., 2006), modeling simulations (Wang et al., 2010), or even satellite retrievals (Jin et al., 2017; Sun et al., 2018), and then examined using three-dimensional chemical transport models (CTMs) (Jiménez et al., 2004; Zhang et al., 2009; Liu et al., 2010; Ye et al., 2016)."

[Comment]: *85: Please define PR and FR..*

[Response]: The PR and FR have been defined in our previous study (Xing et al., 2018). As the reviewer suggested, we provide the reference to clarify the definition of PR and FR in the revised manuscript, as follows.

(Page 4 Line 85-87) "Based on the RSM, the chemical response indicators of Peak Ratio (PR) and Flex Ratio (FR) have been designed to identify regimes of O_3 and $PM_{2.5}$ chemistry, respectively (see Xing et al., 2018 for detailed description of PR and FR)."

Reference:

Xing, J., Ding, D., Wang, S., Zhao, B., Jang, C., Wu, W., Zhang, F., Zhu, Y., and Hao, J. Quantification of the enhanced effectiveness of NOx control from simultaneous reductions of VOC and NH3 for reducing air pollution in the Beijing–Tianjin–Hebei region, China, Atmos. Chem. Phys., 18, 7799-7814, https://doi.org/10.5194/acp-18-7799-2018, 2018.

[Comment]: *101: What is meant be severe here? Are the goals to address severe episodes in the winter or address longer-term annual averages? As the chemical mechanisms driving the former are not well know, yet, my guess is the focus of this article is on the latter, which should be clarified.*

[Response]: We agree with the reviewer that our target focuses on reducing long-term annual averages. To clarify this point, we have changed the "severe pollution" to "air pollution" in the revised manuscript, as follows.

(Page 5 Line 101-103) "Notably, accurate quantification of the nonlinear responses of O_3 and $PM_{2.5}$ to their precursor emissions is critical and a prerequisite for effective mitigation of air pollution in China."

[Comment]: *143 - 146: The cited works here are not published yet, so please provide a brief summary of the performance benchmarks and statistics.*

[Response]: We have updated the two cited papers which have been recently published or sent for publication. As the reviewer suggested, we also summarized the performance statistics in the revised manuscript as follows.

(Page 7 Line 148-152) "The normalized mean biases of CMAQ in predicting $PM_{2.5}$ and O_3 are -16.4% and -12.5% compared with monitoring data obtained from the China National Environmental Monitoring Centre. The mean

fractional biases for $PM_{2.5}$ and O_3 prediction are -14.2% and -11.1%, respectively (within the benchmark of ±60%). The mean fractional errors for $PM_{2.5}$ and O_3 prediction are 21.6% and 17.0% respectively (within the benchmark of 75%)."

Ding, D., Xing, J., Wang, S., Liu, K. and Hao, J.: Estimated Contributions of Emissions Controls, Meteorological Factors, Population Growth, and Changes in Baseline Mortality to Reductions in Ambient PM 2.5 and PM 2.5-Related Mortality in China, 2013–2017. Environmental health perspectives, 127(6), 067009, 2019a.

Ding, D., Xing, J., Wang, S., Chang, X. and Hao, J.: Impacts of emissions and meteorological changes on China's ozone pollution in the warm seasons of 2013 and 2017, Front. Environ. Sci. Eng. 2019, 13(5): 76, 2019b.

[Comment]: *155 - 263: I have questions about the spatial dimension of the terms in these equations. The manuscripts says that Xi was fit for every grid cell. Does that mean that in each grid cell it was known from the CTM simulations how Conc responded to each of the precursor emission species perturbed specifically in that grid cell? Or is it how Conc response to emissions perturbed uniformly throughout the entire model domain? If the former, that seems like a prohibitively large number of model runs (number of grid cells x 40). In this case then the response is the national average response? If the latter, it seems like the applicability of these equations for policy application is hindered by transport, in that it is now known if the change in concentration is occurring owing to changes in emissions in that location or emissions several hundred km upwind. In essence, a map of the response is not equivalent to a map of where the emissions changes need to be to elicit that response, hence this precludes using this information for region-specific changes to precursor emissions. Unless there are policies that aim to uniformly reduce emissions (from all sectors) the same amount throughout the country, it is hard to envision the direct applicability of these relationships for policy. Thus I'm not sure of the value of the province-specific values like those shown in Fig 11– a PR in a particular province isn't necessarily associated with changes to emissions in that province alone.*

[Response]: We thank for the reviewer for raising a critical issue about the spatial match of responding grid cell and controlling grid cell. As the reviewer mentioned, it requires a large number of model runs to identify the controls for each grid cell, which is impossible. Thus, in this study, we applied the same level of emission perturbations to all grid cells across the country. The Xi was still fit for every grid cell, while the control factors represent the emission controls for the whole country, instead of the individual grid cell or region. We agree with the reviewer that the response of PM2.5 and O3 to different regional sources varies significantly. As found in our previous study (Xing et al., 2011), the local NOx controls can have either benefit or dis-benefit in reducing O3, while regional NOx controls usually exhibit benefit in reducing O3. The overall effects are determined by the combination of the selected local/regional control ratios. However, in China, multi-regional joint controls are more likely conducted rather than only controls on a single region. Besides, our previous study also recommended to apply the same local to regional control level for all regions to achieve air quality attainment with the maximal cost-benefit optimization (Xing et al., 2019). The province-specific values shown in Fig 11 provide an estimate of nonlinear response under the uniform-control case, which suggests the additional action needed for each province to avoid potential risk even after considering the multi-regional controls.

To clarify this point, we have added more discussion in the revised manuscript, as follows.

(Page 7, Line 156-161) "Though the responses of O_3 and $PM_{2.5}$ to local or regional emissions vary significantly as suggested in our previous study (Xing et al., 2011), we applied the same change ratio of each pollutant emission

to all regions across China in this study. This approach is consistent with the implementation of a multi-regional joint control strategy, which is reasonable for China. The same level of local and regional emission reduction has been recommended to achieve China's aggressive air quality goals (Xing et al., 2019)."

(Page 22, Line 475-478) "Since the indicators are developed from simulations with spatially uniform emission controls across the country, they are especially useful for providing quick estimates of the potential benefits or risks from uniform controls. These estimates can also provide a basis to design more localized control strategies for particular regions."

Reference:

Xing, J., Wang, S. X., Jang, C., Zhu, Y., and Hao, J. M.: Nonlinear response of ozone to precursor emission changes in China: a modeling study using response surface methodology, Atmospheric Chemistry and Physics, 11, 5027-5044, 10.5194/acp-11-5027-2011, 2011.

Xing, J., Zhang, F., Zhou, Y., Wang, S., Ding, D., Jang, C., Zhu, Y. and Hao, J.: Least-cost control strategy optimization for air quality attainment of Beijing–Tianjin–Hebei region in China. *Journal of environmental management*, *245*, 95-104, 2019.

[Comment]: *Fig 3: Please include units. Also define the domain over which the emissions perturbations are being considered here.*

[Response]: As the reviewer suggested, we have included units ("μg m^{-3}" for $PM_{2.5}$ and "ppb" for O_3), and clarified the emissions perturbations in the caption of Figure 3, as follows.

"Isopleth of population-weighted $PM_{2.5}$ and daytime O_3 to precursor emission change in different months. (The x- and y- axes represent precursor emission rates with a baseline of 1, applied to all grid cells in China; background colors represent the population-weighted $PM_{2.5}$ and daytime O_3 concentrations in China, with units of μg m^{-3} for $PM_{2.5}$ and ppb for O_3)"

[Comment]: *245: I understand why 0 is a lower limit, but why is 2 an upper limit? This seems to cut off a lot of points in April (Fig 5).*

[Response]: We agree with the reviewer that more points will be available for regression if we set the upper limit to be larger than 2. In this study, we set the range of emission changes as 0 to 2 to be consistent with our previous studies in which the pf-RSM performance has been well examined. Also, enlarging the upper limit will increase the sampling space, which might also increase the number of cases used to fit the pf-RSM.

To clarify this point, we have added some discussion in the revised manuscript, as follows.

(Page 8 Line 162-164) "The control matrix is provided in Table S2. The range of emission changes is set as 0 to 2 to be consistent with our previous studies in which the pf-RSM performance has been well examined (Xing et al., 2011; Wang et al., 2011; Xing et al., 2018; Ding et al., 2019b)."

[Comment]: *General: If a metric like FR and AdjGR don't agree, the authors are placing the blame entirely on the observable indicator e.g. AdjGR. However, there is some degree of inaccuracy in FR, related to the extent to which the pf-RSM explains the concentration responses. The authors should thus begin the results section with a summary of the accuracy of Eq 1, particularly in terms of discussing the residuals of this functional fit and their magnitudes, showing plots of the change in concentration predicted by FR or PF vs the actual change in concentrations.*

Next, the magnitude of these residuals should be taken account when considering figures like 4 and 5. I suspect that the distinction of the 4 quadrants in each panel of Figs 4 and 5 directly along the axis is too strict. Rather, corresponding to the magnitude of the residual error in (1), the comparison for Figs 4 and 5 should be to identify points that lie some distance away from the quadrant boundaries, as points near the boundaries could be impacted by the error FR or PF.

Further, it's not clear in the writeup if the change in concentration in Eq 1 is that from the RSM or the CTM – this should be clarified. If the former, then there's an additional source of error that needs to be stated and accounted for, which is the RSM itself.

Lastly, these sources of error should be kept in mind in the presentation of all of the results comparing observable indicator responses vs RMS responses, e.g., discussion of Figs 7, 9, 10, 12

[Response]: We agree with the reviewer that the disagreement between FR and AdjGR can be influenced from uncertainties in both indicators, and it is importance to consider the error of polynomial approximations of the CTM. In the development of pf-RSM, we have examined the performance of pf-RSM to ensure its accuracy to meet the criteria of a mean normalized error within 2% and a maximal normalized error within 10%, comparing against with CMAQ. As we studied the pattern of the residuals (errors), large errors are mostly located in the marginal areas where the emissions were reduced to nearly zero and the concentration will be very small. Thus, the errors in pf-RSM has limited impacts on the shape of nonlinear curve of the response function. However, the uncertainties in the chemical mechanism of CMAQ will also contribute to the bias of O3/PM-chemistry determination. As the reviewer suggested, we have clarified the potential errors existed in CMAQ/RSM, and focused on our discussion on the observable indicators, in the revised manuscript, as follows.

(Page 8 Line 163-170) "The pf-RSM performance in predicting $PM_{2.5}$ and O_3 responses has been evaluated in detail using leave-one-out cross validation as well as the out-of-sample validation method, with normalized errors all within 5% for both $PM_{2.5}$ and O_3 across the domain. Relatively large biases occurred for marginal cases, where emissions are controlled by nearly 100% and predicted concentrations are very small. These cases have limited influence on the shape of nonlinear curve of the response function. However, the RSM is developed from a suite of CMAQ simulations, and so uncertainties in the chemical mechanism used in CMAQ might influence the O_3 and $PM_{2.5}$ predictions."

(Page 22 Line 491-495) "We note that the discrepency between the observable indicator and the responsive indicator might also be influcenced by uncertainties in the chemical mechanism of CMAQ as well as prediction errors of the pf-RSM. The new indicators were designed based on the existing chemical mechanism, and the transition values might be refined in the future as our understanding of atmospheric chemical processes improves."

[Comment]: *201: As defined as the ratio of VOCs to NOx, it seems rather circuitous to derive this equation only to show that it reduces to the ratio of the coefficients for the linear VOC and NOx terms (i.e. x5/x6).*

[Response]: The ratio of VOCs to NOx (VNr) is designed as the level of simultaneous control of VOCs to prevent an increase in O_3 levels from the NOx controls when PR<1 (VOC-limited). Thus we defined the VNr equals the ΔEvoc/ΔEnox which makes first derivative of the ΔConcO3 to ΔEnox equal 0. In the polynomial function of O3 response to emissions, the first derivative of the ΔConcO3 to ΔEnox (ΔEso2, ΔEnh3 are 0, while ΔVOC is r× ΔEnox) is written as follows.

$$5 * \mathrm{X}_1 * \Delta E_{NOx}{}^4 + 4 * \mathrm{X}_2 * \Delta E_{NOx}{}^3 + 3 * \mathrm{X}_3 * \Delta E_{NOx}{}^2 + 2 * \mathrm{X}_4 * \Delta E_{NOx} + \mathrm{X}_5 + \mathrm{X}_6 * \mathrm{r} + 2 * \mathrm{X}_7 * \mathrm{r}^2 * \Delta E_{NOx} + 3 * \mathrm{X}_8 * \mathrm{r}^3 * \Delta E_{NOx}{}^2 + 2 * \mathrm{X}_9 * \mathrm{r} * \Delta E_{NOx}{}^2 + 4 * \mathrm{X}_{10} * \mathrm{r}^3 * \Delta E_{NOx}{}^3 + 6 * \mathrm{X}_{11} * \mathrm{r} * \Delta E_{NOx}{}^5 + 3 * \mathrm{X}_{12} * \mathrm{r} * \Delta E_{NOx}{}^2 = 0$$

Considering the NOx controls will be taken from baseline and ΔEnox is close to 0, we ignore the terms of ΔEnox in the first derivative function above, then it can be written as follows,

$$\mathrm{X}_5 + \mathrm{X}_6 * \mathrm{r} = 0$$

Therefore, the VNr reduces to the ratio of the coefficients for the linear VOC and NOx terms.

We agree with the reviewer that the original description about VNr calculation is a bit ambiguous. We have clarified it in the revised manuscript as follows.

(Page 10 Line 219-231) "This level is defined by the ratio of VOCs to NO_x (i.e., VNr) corresponding to the PR and is calculated as follows:

$$VNr = r|_{\frac{\partial \Delta Conc_{O3}}{\partial \Delta E_{NOx}}=0} \quad when\ PR < 1 \quad , r = {}^{\Delta E_{VOC}}/_{\Delta E_{NOx}} \qquad (4)$$

where $\frac{\partial \Delta Conc_{O3}}{\partial \Delta E_{NOx}}$ is the first derivative of the $\Delta Conc_{O3}$ to ΔE_{NOx}. When $\Delta E_{VOC} = r \times \Delta E_{NOx}$, and ΔE_{SO2} and ΔE_{NH3} are 0, $\frac{\partial \Delta Conc_{O3}}{\partial \Delta E_{NOx}}$ can be written as follows:

$$5 * \mathrm{X}_1 * \Delta E_{NOx}{}^4 + 4 * \mathrm{X}_2 * \Delta E_{NOx}{}^3 + 3 * \mathrm{X}_3 * \Delta E_{NOx}{}^2 + 2 * \mathrm{X}_4 * \Delta E_{NOx} + \mathrm{X}_5 + \mathrm{X}_6 * \mathrm{r} + 2 * \mathrm{X}_7 * \mathrm{r}^2 * \Delta E_{NOx} + 3 * \mathrm{X}_8 * \mathrm{r}^3 * \Delta E_{NOx}{}^2 + 2 * \mathrm{X}_9 * \mathrm{r} * \Delta E_{NOx}{}^2 + 4 * \mathrm{X}_{10} * \mathrm{r}^3 * \Delta E_{NOx}{}^3 + 6 * \mathrm{X}_{11} * \mathrm{r} * \Delta E_{NOx}{}^5 + 3 * \mathrm{X}_{12} * \mathrm{r} * \Delta E_{NOx}{}^2 = 0 \qquad (5)$$

Since the ΔE_{NOx} is close to 0 when the controls are taken from the baseline, we ignore the terms of ΔE_{NOx} in the first derivative function above, then it can be written as follows,

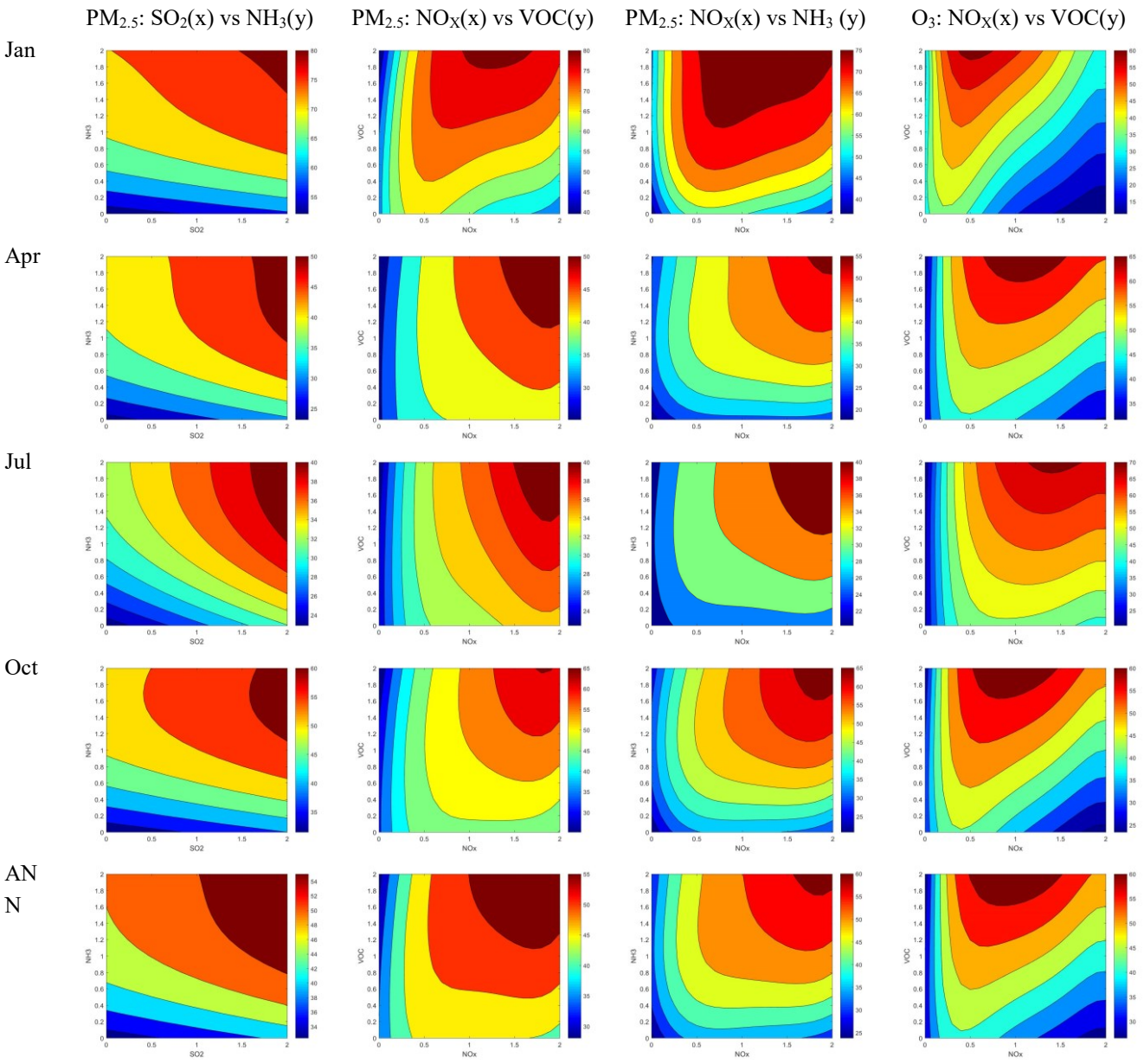
$$\mathrm{X}_5 + \mathrm{X}_6 * \mathrm{r} = 0 \qquad (6)$$

The VNr therefore can be calculated using the following equation:

$$VNr = -\frac{\mathrm{X}_5}{\mathrm{X}_6} \qquad (7)"$$

[Comment]: *228: It is interesting that this change reduces down to just the linear response coefficient of PM2.5 with respect to NH3. This makes me want to see an additional plot in Fig 3 which is NH3 vs NOx.*

[Response]: As the reviewer suggested, we have provided the $PM_{2.5}$ response to NH_3 and NOx in the Fig 3, as follows.



[Comment]: *275: Why is there a seasonal dependence to the performance of HCHO/NO2, particularly with such low performance in April?*

[Response]: The seasonality of performance of the observable indicators (such as HCHO/NO2) in predicting O3 chemistry might be associated with the uncertainty of the transition values, as different transition values were reported by different studies or for different location and time (Zhang et al., 2009). In this study, we found that

the performance of the HCHO/NO2 can be substantially improved by using the transition value of 0.5 instead of 1, as shown in Table 2. Such result also implies that those indicators by using concentrations of just two species cannot fully consider all factors that determine the O3 chemistry.

To clarify this point, we have added some discussion in the revised manuscript, as follows.

(Page 14 Line 301-305) "However, the performance of HCHO/NO_y and HCHO/NO_2 could be greatly improved by using lower transition values, with increased annual success rates as high as 76 %. The change of the transition values implies that such indicators cannot fully consider all factors that determine the O_3 chemistry by using concentrations of just two species."

Reference:

Zhang, Y., Wen, X. Y., Wang, K., Vijayaraghavan, K., and Jacobson, M. Z.: Probing into regional O-3 and particulate matter pollution in the United States: 2. An examination of formation mechanisms through a process analysis technique and sensitivity study, Journal of Geophysical Research-Atmospheres, 114, 31, 10.1029/2009jd011900, 2009.

[Comment]: *384: Could the authors comment on the practicality of this application? I'm having a hard time imagining simultaneous equal %-based reductions to China-wide NH3 and NOx emissions resulting from any real policy, given that these would be coming largely from different sectors, in different locations.*

[Response]: We understand the reviewer's concern that the control strategy may not be uniform across the country, since it is impossible to require all regions to follow the same reduction rates, even though it might be cost-efficient for long term air quality attainment (Xing et al., 2019). However, the indicator-based approach, which uses the ambient concentrations of only a few species, can quickly estimate the potential benefit or risk from the uniform controls, which can act as a basis to design more localized control strategies for particular regions. For example, additional simultaneous VOC control with NOx is recommended in regions located at VOC-limited regime.

As the reviewer suggested, we have provided some discussion about the usage of indicator in the revised manuscript, as follows.

(Page 22 Line 476-479) "Since the indicators are developed from simulations with spatially uniform emission controls across the country, they are especially useful for providing quick estimates of the potential benefits or risks from uniform controls. These estimates can also provide a basis to design more localized control strategies for particular regions."

Reference:

Xing, J., Zhang, F., Zhou, Y., Wang, S., Ding, D., Jang, C., Zhu, Y. and Hao, J.: Least-cost control strategy optimization for air quality attainment of Beijing–Tianjin–Hebei region in China. *Journal of environmental management*, *245*, 95-104, 2019.

[Comment]: *420: What are the control pathways considered here? Ah â˘A ˘T ok they are mentioned in the figure caption but it would be useful to add to the text.*

[Response]: The control pathways considered here are six types of VOC-to-NOx control ratios, including 0, 0.2, 0.4, 0.6, 0.8 and 1.0. As the reviewer suggested, we have added such information in the revised manuscript as follows.

(Page 20 Line 445-447) "To explore the cobenefits of reducing O_3 and $PM_{2.5}$ after simultaneous control of NO_x and VOCs, we investigated the effectiveness of six control pathways with various VOC-to-NO_x ratios including 0, 0.2, 0.4, 0.6, 0.8 and 1.0 (Fig. 14)."

[Comment]: *Fig 14: It's not clear to me how these results show that simultaneous reductions of O3 and PM2.5 are possible in January – as stated in the text. Rather, it looks like they are not except for all but one scenario (NOx:VOC = 1:1, only at the far end of the pathway). Potentially a very interesting figure here but it needs more explanation.*

[Response]: Due to the strong NO_x-saturated regime in January, compared to other months, a much larger VOC-to-NOx control ratio and greater NOx emission controls are required to prevent potential disbenefits from NOx controls and to achieve simultaneous reductions of O3 and PM2.5. As demonstrated in Figure 14(a), there is only one pathway that can meet the simultaneous reductions of O3 and PM2.5 (i.e., that with VOC-to-NOx equal to 1 and at the far end of the pathway, with greater emission controls).

As the reviewer suggested, we have provided additional explanation about Figure 14 in the revised manuscript as follows.

(Page 20 Line 447-456) "In general, O_3 and $PM_{2.5}$ concentrations can be reduced in all months through simultaneous control of NO_x and VOC emissions, although different VNr and control levels are required in different months. In January (under strongly NO_x-saturated conditions), reductions in $PM_{2.5}$ and O_3 require VOC emission controls in addition to NOx controls to prevent potential disbenefits associated with the nonlinear chemistry. The smaller VNr required for $PM_{2.5}$ (~0.4) than for O_3 (~1.0) in this case might be associated with the smaller PR for $PM_{2.5}$ as well as the additional benefit of VOC controls in reducing secondary organic aerosols. Apparently, a larger VNr control ratio and greater emission control is required in January compared with other months. In Fig. 14(a), only one pathway can achieve simultaneous reduction in O_3 and $PM_{2.5}$ concentrations (i.e., the pathway with VNr equal to 1 and at the far end of the pathway, with reduction rates > 80%)."

[Comment]: *37: subscript on NOx.*

[Response]: We have corrected it in the revised manuscript.

[Comment]: *51: Seinfeld et al. 2017 not in bibliography. Did the authors mean Seinfeld and Pandis (2012)?*

[Response]: We are sorry for the typo. We have updated the reference to “Seinfeld and Pandis, 2012” in the revised manuscript.

[Comment]: *407 - 410: There is perhaps a word missing or something from this sentence, please check.*

[Response]: As the reviewer suggested, we have revised this sentence in the revised manuscript as follows.

(Page 20 Line 433-436) “The PR results suggest strong NO_x-saturated regimes in northern and eastern China including key regions such as the Sichuan Basin, YRD, and PRD, where simultaneous VOC control with a certain VOC-to-NO_x ratio is required to prevent increases in O_3 levels from the NO_x controls.”

Development and application of observable response indicators for design of an effective ozone and fine particle pollution control strategy in China

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Abstract

Designing effective control policies requires efficient quantification of the nonlinear response of air pollution to emissions. However, neither the current observable indicators nor the current indicators based on response-surface modeling (RSM) can fulfill this requirement. Therefore, this study developed new observable RSM-based indicators and applied them to ambient fine particle ($PM_{2.5}$) and ozone (O_3) pollution control in China. The performance of these observable indicators in predicting O_3 and $PM_{2.5}$ chemistry was compared with that of the current RSM-based indicators. H_2O_2×HCHO/NO_2 and total ammonia ratio, which exhibited the best performance among indicators, were proposed as new observable O_3- and $PM_{2.5}$-chemistry indicators, respectively. Strong correlations between RSM-based and traditional observable indicators suggested that a combination of ambient concentrations of certain chemical species can serve as an indicator to approximately quantify the response of O_3 and $PM_{2.5}$ to changes in precursor

emissions. The observable RSM-based indicator for O_3 (observable peak ratio) effectively captured the strong NO_x-saturated regime in January and the NO_x-limited regime in July, as well as the strong NO_x-saturated regime in northern and eastern China and their key regions, including the Yangtze River Delta and Pearl River Delta. The observable RSM-based indicator for $PM_{2.5}$ (observable flex ratio) also captured strong NH_3-poor condition in January and NH_3-rich condition in April and July, as well as NH_3-rich in northern and eastern China and the Sichuan Basin. Moreover, analysis of these newly developed observable response indicators suggested that the simultaneous control of NH_3 and NO_x emissions produces greater benefits in provinces with higher $PM_{2.5}$ exposure by up to 12 μg m^{-3} $PM_{2.5}$ per 10 % NH_3 reduction compared with NO_x control only. Control of volatile organic compound (VOC) emissions by as much as 40 % of NO_x controls is necessary to obtain the co-benefits of reducing both O_3 and $PM_{2.5}$ exposure at the national level when controlling NO_x emissions. However, the VOC-to-NO_x ratio required to maintain benefits varies significantly from 0 to 1.2 in different provinces, suggesting that a more localized control strategy should be designed for each province.

Keywords: nonlinear response, precursor emissions, response surface model, ozone, $PM_{2.5}$, indicator

1. Introduction

Air pollution has attracted great attention because of its harmful effects on human health (Cohen et al., 2017), climate (Myhre et al., 2013), agriculture and ecosystems (Fuhrer et al., 2016), and visibility (Friedlander et al., 1977). In particular, ambient fine particles ($PM_{2.5}$) and ozone (O_3) are among the top risk factors for global mortality (Forouzanfar et al., 2015; Cohen et al., 2017) and have increased the need to effectively control anthropogenic sources in order to reduce the ambient concentrations of $PM_{2.5}$ and O_3 (Wang et al., 2017). The challenge is that the dominant contributions to ambient $PM_{2.5}$ and O_3 arise from a series of chemical reactions among precursors, including sulfur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3) and volatile organic compounds (VOCs) (Seinfeld and Pandis, 2012). The complexity of the chemical reactions and pathways associated with variations in meteorological conditions and precursor levels results in strong nonlinear responses of $PM_{2.5}$ and O_3 to their precursor emission changes (West et al., 1999; Hakami et al., 2004; Cohan et la., 2005; Pun et al., 2007; Megaritis et al., 2013). Such nonlinearity issues are a major challenge for policy-makers to design an effective control strategy.

Chemical species in the atmosphere are often highly correlated with one another, since their concentrations are affected by common atmospheric physical processes (e.g., mixing and transport) and chemical reactions. Concentrations of pollutants such as O_3 and $PM_{2.5}$ are typically determined based on the ambient levels of their gaseous precursors, implying that O_3 and $PM_{2.5}$ chemistry can be identified through a combination of concentrations of some of their related chemical species (i.e., indicators). The empirical kinetic modeling approach (EKMA) developed by the U.S. EPA quantifies the relationships of O_3 with its precursor concentrations based on O_3 chemistry (Freas et al., 1978; Gipson et al., 1981). The EKMA plot can aid inference of control strategy effectiveness (e.g., NO_x or VOC control) according to VOC-to-NO_x ratios. Several studies have developed "observable" indicators by relating O_3 to reactive

nitrogen concentrations and species related to atmospheric oxidation. Such indicators include NO_y, H_2O_2/HNO_3, $HCHO/NO_2$ and $H_2O_2/(O_3+NO_2)$ (Milford et al., 1994; Sillman, 1995; Tonnesen and Dennis, 2000; Sillman and He, 2002), which can be used to identify NOx-saturated or -limited regimes. The O_3 indicators can be derived from surface-monitoring observations (Peng et al., 2006), modeling simulations (Wang et al., 2010), or even satellite retrievals (Jin et al., 2017; Sun et al., 2018), and then examined using three-dimensional chemical transport models (CTMs) (Jiménez et al., 2004; Zhang et al., 2009; Liu et al., 2010; Ye et al., 2016). Regarding $PM_{2.5}$ chemistry (more specifically for inorganic $PM_{2.5}$ sensitivities to NH_3 and NO_x), indicators such as the degree of sulfate neutralization (DSN), gas ratio (GR), and adjusted gas ratio (AdjGR) have been developed (defined in Text S1) to identify NH_3-poor or -rich conditions (Ansari and Pandis, 1998; Takahama et al., 2004; Pinder et al., 2008; Dennis et al., 2008). The indicator-based method can be efficient in determining the chemical regime in the current scenarios and in qualitatively estimating O_3 and $PM_{2.5}$ sensitivities to small perturbations in precursor emissions or ambient concentrations without involving complex CTMs. However, traditional indicator methods are unable to quantify the extent of the chemistry regime (Pinder et al., 2008); hence, the traditional observable indicators provide policy-makers limited information for reducing O_3 and $PM_{2.5}$ pollution.

The sensitivity of O_3 and $PM_{2.5}$ to precursor emissions can be explored by running multiple brute-force CTM simulations. For instance, the response surface model (RSM) developed from brute-force simulations can generate a wide range of O_3 and $PM_{2.5}$ responses to precursor emissions ranging from fully controlled to doubled emissions (i.e., -100 % to 100 % change relative to the baseline emission) (Xing et al., 2011; Wang et al., 2011). Based on the RSM, the chemical response indicators of Peak Ratio (PR) and Flex Ratio (FR) have been designed to identify regimes of O_3 and $PM_{2.5}$ chemistry, respectively (see Xing et al., 2018 for detailed description of PR and FR). In contrast to the observable indicators, the PR and FR are meaningful values that represent the exact transition point at which a chemistry regime

converts to another regime. With the recent development of the polynomial function-based RSM (pf-RSM), the PR and FR can be easily calculated (Xing et al., 2018). However, this method is built on at least 20 CTM simulations; in other words, the estimating the PR and FR requires considerable computing resources. As a result, RSM use remains limited despite recent improvements in RSM efficiency (Xing et al., 2017).

Over the preceding decade, China's air quality has undergone substantial changes. In particular, the enactment of the *Air Pollution Prevention and Control Action Plan* from 2013 to 2017 greatly reduced $PM_{2.5}$ exposure (Zhao et al., 2018; Ding et al., 2019a). However, during this period, significant increases in O_3 concentrations were observed in most Chinese cities (Li et al., 2018). The rate of increase in O_3 concentration (based on the 90th percentile of daily maximum of 8-hr running average) was approximately 27 %, 19 %, and 8 % in the North China Plain (NCP), Yangtze River Delta (YRD), and Pearl River Delta (PRD), respectively (Ding et al., 2019b). Greater control over anthropogenic sources must be enforced to reduce $PM_{2.5}$ and O_3 concentrations (Lu et al., 2018). Notably, accurate quantification of the nonlinear responses of O_3 and $PM_{2.5}$ to their precursor emissions is critical and a prerequisite for effective mitigation of air pollution in China.

The design of an effective O_3 and $PM_{2.5}$ control strategy requires efficient quantification of air pollutant sensitivity to precursor emissions. Indicator studies have demonstrated that the nonlinear response of O_3 and $PM_{2.5}$ to precursors can be estimated by using ambient concentrations of related chemical species. It is expected that the response indicators originally derived from RSM predictions (i.e., PR and FR) can also be calculated using a combination of ambient concentrations of certain chemical species, enabling these indicators to become "observable" indicators rather than being dependent on numerous CTM simulations. To support the needs of policy design for O_3 and $PM_{2.5}$ control, this study developed effective indicators that not only represent O_3 and $PM_{2.5}$ chemistry but also aid in determining

the most feasible emission reduction path, similar to the benefits provided by RSM-based indicators. The flow of this study is presented in Fig. 1. The new observable response indicators were developed by investigating the link between observable and RSM-based indicators in China.

The remainder of this paper is structured as follows: Section 2 presents the detailed methods for CTM modeling, RSM configuration and response indicator development. Section 3 presents the evaluation of the performance of observable indicators in predicting the chemistry regime and the development of the observable response indicators and discusses their policy implications. Section 4 summarizes the main conclusions of this study.

2. Method

2.1. Configuration of the CTM and RSM

In this study, the Community Multi-scale Air Quality (CMAQ) model (version 5.2) was used to simulate the baseline concentrations of O_3 and $PM_{2.5}$ and their responses in numerous emission control scenarios with different emission change ratios. The simulation was conducted on a domain covering China with 27 km × 27 km horizontal resolution (Fig. 2). In 2017, January, April, July, and October were simulated to represent winter, spring, summer, and fall, respectively. An annual level was estimated as the average of the levels in these four months. The concentration data was analyzed based on the monthly average for afternoon O_3 (12:00–18:00 China Standard Time when O_3 was the highest across a day), and monthly average for 24-h $PM_{2.5}$. To approximate exposure concentrations, we also estimated population-weighted O_3 and $PM_{2.5}$ at the regional or national level by averaging the gridded concentrations weighted by the population in each grid cell. The gridded population data were obtained from the 1 km × 1 km LandScan population dataset in 2016 (Oak Ridge National Laboratory, 2013).

The anthropogenic emission data were developed by Tsinghua University by using a bottom-up method (Ding et al., 2019a), with updated activity data from the 2017 China statistical yearbook as well

as the latest application rates of end-of-pipe control technologies based on the governmental bulletin and reports. The anthropogenic emissions were gridded into 27 km × 27 km horizontal resolution to match the CMAQ model (Fig. S1). The 2017 biogenic emissions over China were generated using the Model for Emissions of Gases and Aerosols from Nature (MEGAN; version 2.04). The meteorology field, driven by the Weather Research and Forecasting Model (WRF; version 3.7), followed the same configuration as that in our previous study (Ding et al., 2019a,b), and thus included the Morrison double-moment microphysics scheme, the RRTMG radiation scheme, Kain-Fritsch cumulus cloud parameterization, the Pleim-Xiu land-surface physics scheme, and the ACM2 PBL physics scheme. We used NCEP FNL (Final) Operational Global Analysis data for the initial and boundary conditions in the WRF. The comparison with observation data from the National Climatic Data Center suggested agreeable performance of the WRF model for simulating wind speed, humidity and temperature (Table S1). The CMAQ model performance in reproducing O_3 and $PM_{2.5}$ concentrations was evaluated by comparison with the ground-based observations (Fig. S2), which suggested acceptable CMAQ model performance that met the recommended benchmark (Ding et al., 2019a,b). The normalized mean biases of CMAQ in predicting $PM_{2.5}$ and O_3 are -16.4% and -12.5% compared with monitoring data obtained from the China National Environmental Monitoring Centre. The mean fractional biases for $PM_{2.5}$ and O_3 prediction are -14.2% and -11.1%, respectively (within the benchmark of ±60%). The mean fractional errors for $PM_{2.5}$ and O_3 prediction are 21.6% and 17.0% respectively (within the benchmark of 75%). The RSM was developed based on multiple CTM simulations for various emission-control scenarios according to the brute-force method. Identical to our previous RSM studies (Xing et al., 2017, 2018), the responses of O_3 and $PM_{2.5}$ to precursor emissions were analyzed using the baseline case and 40 control scenarios using the Latin Hypercube Sample method for four control variables, namely the emission ratios of NO_x, SO_2, NH_3, and VOCs. Though the responses of O_3 and $PM_{2.5}$ to local or regional emissions vary significantly as suggested in our previous study (Xing

et al., 2011), we applied the same change ratio of each pollutant emission to all regions across China in this study. This approach is consistent with the implementation of a multi-regional joint control strategy, which is reasonable for China. The same level of local and regional emission reduction has been recommended to achieve China's aggressive air quality goals (Xing et al., 2019).

The control matrix is provided in Table S2. The range of emission changes is set as 0 to 2 to be consistent with our previous studies in which the pf-RSM performance has been well examined (Xing et al., 2011; Wang et al., 2011; Xing et al., 2018; Ding et al., 2019b). The pf-RSM performance in predicting $PM_{2.5}$ and O_3 responses has been evaluated in detail using leave-one-out cross validation as well as the out-of-sample validation method, with normalized errors all within 5% for both $PM_{2.5}$ and O_3 across the domain. Relatively large biases occurred for marginal cases, where emissions are controlled by nearly 100% and predicted concentrations are very small. These cases have limited influence on the shape of nonlinear curve of the response function. However, the RSM is developed from a suite of CMAQ simulations, and so uncertainties in the chemical mechanism used in CMAQ might influence the O_3 and $PM_{2.5}$ predictions.

2.2. RSM-based indicators of O_3 and $PM_{2.5}$ chemistry

Based on the developed pf-RSM, the nonlinear responses of O_3 and $PM_{2.5}$ concentrations to precursor emissions can be represented as follows:

$$\Delta Conc = \sum_{i=1}^{n} X_i \cdot (\Delta E_{NOx})^{a_i} \cdot (\Delta E_{SO2})^{b_i} \cdot (\Delta E_{NH3})^{c_i} \cdot (\Delta E_{VOCs})^{d_i} \quad (1)$$

where $\Delta Conc$ is the change in O_3 or $PM_{2.5}$ concentration from the baseline concentration calculated from a polynomial function of four variables (ΔE_{NOx}, ΔE_{SO2}, ΔE_{NH3}, ΔE_{VOCs}); ΔE_{NOx}, ΔE_{SO2}, ΔE_{NH3}, and ΔE_{VOCs} are the change ratios of NO_x, SO_2, NH_3, and VOC emissions (i.e., *ΔEmissions* / *Baseline_Emissions*), respectively, relative to the baseline emissions (baseline = 0); and a_i, b_i, c_i, and d_i are the nonnegative integer powers of ΔE_{NOx}, ΔE_{SO2}, ΔE_{NH3}, and ΔE_{VOCs}, respectively. X_i is the coefficient of term *i* for the 14

(n) terms listed in Table 1.

The terms used to represent $PM_{2.5}$ and O_3 responses were determined in designing the pf-RSM (Table 1). The high-degree terms of NO_x, VOCs and NH_3 represent their strong nonlinear contributions to O_3 or $PM_{2.5}$. The interaction terms of NO_x and VOC for $PM_{2.5}$ and O_3 represent the nonlinearity in atmospheric oxidations, whereas those of NO_x and NH_3 for $PM_{2.5}$ represent aerosol thermodynamics (Xing et al., 2018).

X_i was fitted by 40 CTM control scenarios for each spatial grid cell. The X_i values in the pf-RSM for annual-averaged population-weighted O_3 and $PM_{2.5}$ concentrations in 31 provinces in China are provided in Table S3 and Table S4, respectively. The terms with first degree for NOx, SO_2, NH_3, and VOCs represent the first derivative of $PM_{2.5}$ and O_3 response to each precursor emission. O_3 was more sensitive to NO_x (term X_5) and VOCs (term X_6) than to SO_2 (term X_{13}) or NH_3 (term X_{14}), and O_3 sensitivity was negative to NO_x but positive to VOCs in most provinces. $PM_{2.5}$ sensitivities to the four precursors (terms X_1, X_2, X_5 and X_{11} for VOCs, NH_3, SO_2, and NO_x, respectively) were comparable, whereas $PM_{2.5}$ sensitivity to NO_x could be negative or positive.

The nonlinearities of O_3 and $PM_{2.5}$ to precursors were mainly determined by high-order and interaction terms. To illustrate such nonlinearities further, we used a series of isopleths, as shown in Fig. 3, as an example to present the national-averaged $PM_{2.5}$ response to SO_2 and NH_3, NO_x and NH_3, as well as $PM_{2.5}$ and O_3 responses to NO_x and VOCs in different months. Strong nonlinearity was noted in $PM_{2.5}$ sensitivity to NH_3, and in O_3 and $PM_{2.5}$ sensitivities to NO_x. $PM_{2.5}$ sensitivity to NH_3 increased alongside the transition of $PM_{2.5}$ chemistry from the NH_3-rich condition (typically at high NH_3 emission ratios) to the NH_3-poor condition (typically at low NH_3 emission ratios). O_3 and $PM_{2.5}$ sensitivities to NO_x were negative under the NO_x-saturated regime (typically at high NO_x emission ratios) but became positive under the NO_x-limited regime (typically at low NO_x emission ratios). In addition, the transition points

(corresponding to the NO_x or NH_3 ratios at which the chemical regime for O_3 or $PM_{2.5}$ chemistry changed) varied by time (Fig. 3) and space (see the isopleths at different provinces in Figs S3-S6). In general, the NH_3-poor condition appears in winter because of low NH_3 evaporation and little agriculture activity which is a dominant NH_3 source. The strong NO_x-saturated condition appears in winter when photolysis is less active than in other seasons, and concentrates in industrial regions with abundant NO_x emissions.

To further quantify the aforementioned nonlinearity, two RSM-based response indicators (i.e., the PR for O_3 and FR for $PM_{2.5}$) were calculated as described in our previous studies (Xing et al., 2011, 2018; Wang et al., 2011).

For O_3, the PR can be directly calculated as follows:

$$PR = 1 + \Delta E_{NOx}|_{\frac{\partial \Delta Conc_{O3}}{\partial \Delta E_{NOx}}=0} \quad E_{NOx} \epsilon [a, b] \qquad (2)$$

where $\frac{\partial \Delta Conc_{O3}}{\partial \Delta E_{NOx}}$ is the first derivative of the $\Delta Conc_{O3}$ to ΔE_{NOx}, which can be derived as follows:

$$5 * X_1 * \Delta E_{NOx}{}^4 + 4 * X_2 * \Delta E_{NOx}{}^3 + 3 * X_3 * \Delta E_{NOx}{}^2 + 2 * X_4 * \Delta E_{NOx} + X_5 = 0 \quad (3)$$

The PR is the NO_x emissions (represented as $1 + \Delta E_{NOx}$) that produce maximum O_3 concentration under the baseline VOC emissions. For PR < 1, the baseline condition is NO_x saturated, and the level of simultaneous control of VOCs to prevent an increase in O_3 levels from the NO_x controls must be understood. This level is defined by the ratio of VOCs to NO_x (i.e., VNr) corresponding to the PR and is calculated as follows:

$$VNr = r|_{\frac{\partial \Delta Conc_{O3}}{\partial \Delta E_{NOx}}=0} \quad when\ PR < 1 \quad , r = {}^{\Delta E_{VOC}}/_{\Delta E_{NOx}} \qquad (4)$$

where $\frac{\partial \Delta Conc_{O3}}{\partial \Delta E_{NOx}}$ is the first derivative of the $\Delta Conc_{O3}$ to ΔE_{NOx}. When $\Delta E_{VOC} = r \times \Delta E_{NOx}$, and ΔE_{SO2} and ΔE_{NH3} are 0, $\frac{\partial \Delta Conc_{O3}}{\partial \Delta E_{NOx}}$ can be written as follows:

$$5 * X_1 * \Delta E_{NOx}{}^4 + 4 * X_2 * \Delta E_{NOx}{}^3 + 3 * X_3 * \Delta E_{NOx}{}^2 + 2 * X_4 * \Delta E_{NOx} + X_5 + X_6 * r + 2 * X_7 *$$

$$r^2 * \Delta E_{NOx} + 3 * X_8 * r^3 * {\Delta E_{NOx}}^2 + 2 * X_9 * r * {\Delta E_{NOx}}^2 + 4 * X_{10} * r^3 * {\Delta E_{NOx}}^3 + 6 * X_{11} * r * {\Delta E_{NOx}}^5 + 3 * X_{12} * r * {\Delta E_{NOx}}^2 = 0 \quad (5)$$

Since the ΔE_{NOx} is close to 0 when the controls are taken from the baseline, we ignore the terms of ΔE_{NOx} in the first derivative function above, then it can be written as follows,

$$X_5 + X_6 * r = 0 \quad (6)$$

The VNr therefore can be calculated using the following equation:

$$VNr = -\frac{X_5}{X_6} \quad (7)$$

For $PM_{2.5}$, the FR can be directly calculated from the polynomial function of $PM_{2.5}$ by estimating the second derivative of the $PM_{2.5}$ response to NH_3 emissions without considering interaction with other pollutants (Xing et al., 2018). In this study, we selected a simplified method to calculate the FR, estimated as the corresponding NH_3 emission ratio when the $PM_{2.5}$ sensitivity to NH_3 and NO_x emissions is equal under the baseline conditions (similar to the definition in Wang et al (2011), but here we calculated the sensitivity of $PM_{2.5}$ instead of nitrate in this study):

$$FR = 1 + \Delta E_{NH3}|_{\frac{\partial \Delta Conc_{PM}}{\partial \Delta E_{NH3}} = \frac{\partial \Delta Conc_{PM}}{\partial \Delta E_{NOx}}} \quad \Delta E_{NH3} \epsilon [a, b], \Delta E_{NOx} = 0, \quad (8)$$

where $\frac{\partial \Delta Conc_{PM}}{\partial \Delta E_{NH3}}$ and $\frac{\partial \Delta Conc_{PM}}{\partial \Delta E_{NOx}}$ are the first derivatives of the $\Delta Conc_{PM}$ to ΔE_{NH3} and ΔE_{NOx}, respectively, and ΔE_{NH3} can be obtained as follows:

$$3 * X_4 * {\Delta E_{NH3}}^2 + (2 * X_3 - X_{10}) * \Delta E_{NH3} + X_2 - X_{11} = 0 \quad (9)$$

The FR is the NH_3 emissions (represented as $1 + \Delta E_{NH3}$) that correspond to the inflection point between NH_3-rich and -poor conditions under baseline NOx emissions. A FR greater than 1 indicates that the baseline condition is NH_3 poor, and a FR less than 1 indicates that the baseline condition is NH_3 rich. The extra benefit in $PM_{2.5}$ reduction (denoted as ΔC_NH_3) from simultaneous NH_3 controls in the same percentage as the required NO_x controls can be quantified as follows:

$$\Delta C\_NH_3 = \left(\frac{\partial \Delta Conc_{PM2.5}}{\partial \Delta E_{NOx}}|_{\Delta E_{NH3}=\Delta E_{NOx}}\right) - \left(\frac{\partial \Delta Conc_{PM2.5}}{\partial \Delta E_{NOx}}|_{\Delta E_{NH3}=0}\right) \quad (10)$$

where

$\frac{\partial \Delta Conc_{PM2.5}}{\partial \Delta E_{NOx}}|_{\Delta E_{NH3}=\Delta E_{NOx}}$ is the first derivative of the $\Delta Conc_{PM2.5}$ response to ΔE_{NOx} when $\Delta E_{NH3} = \Delta E_{NOx}$, and

$\frac{\partial \Delta Conc_{PM2.5}}{\partial E_{NOx}}|_{E_{NH3}=0}$ is the first derivative of the $\Delta Conc_{PM2.5}$ response to ΔE_{NOx} when $\Delta E_{NH3} = 0$.

ΔC_NH_3 can be calculated as follows:

$$\Delta C\_NH_3 = X_2 \quad (11)$$

2.3. Observable indicators of O_3 and $PM_{2.5}$ chemistry

Zhang et al. (2009) summarized the various observable indicators with their corresponding transition values to identify O_3 and $PM_{2.5}$ chemistry: O_3 indicators were H_2O_2/HNO_3, $H_2O_2/(O_3+NO_2)$, NO_y, O_3/NO_x, O_3/NO_y, O_3/NO_z, $HCHO/NO_y$, and $HCHO/NO_2$, and the $PM_{2.5}$ indicators were the DSN, GR, and AdjGR (defined in Text S1); these indicators have been used extensively in previous research (Liu et al., 2010; Wang et al., 2011; Ye et al., 2016). In the current study, we evaluated all the aforementioned indicators except DSN (DSN is included in the definition of the AdjGR, thus it was not considered as a separate indicator in this study). The orignal transition values, summarized by Zhang et al (2009), are listed in Table 2. In the present study, we examined these transition values and compared their performance in predicting O_3 and $PM_{2.5}$ chemistry. Because the RSM-based indicators, PR and FR, are calculated using the multiple CTM simulations that use state-of-the-science representations of O_3 and $PM_{2.5}$ chemistry, these indicators were assumed to represent the true condition for comparison with the condition predicted using observable indicators. The performance of each observable indicator is described by its success rate, which is the ratio of the number of correct predictions to the total number of predictions. A correct prediction is indicated by the observable indicator providing consistent results for O_3 or $PM_{2.5}$ chemistry

as suggsted by PR or FR. The comparison is only conducted for spatial grid cells with valid PR or FR values within the range of 0 (fully controlled emissions) to 2 (double emissions).

As RSM-based indicators, the PR and FR have meaningful values that can be used to illustrate the extent of the chemistry regime. The linkage of observable indicators with the PR and FR was investigated by performing a linear-log regression of the value of the original observable indicator and the values of the PR or FR as follows:

$$log(Y) = A \cdot X + B \qquad (12)$$

where Y is an observable indicator for O_3 or $PM_{2.5}$, X is the RSM-based indicator (i.e., PR for O_3 or FR for $PM_{2.5}$), and the coefficients A and B are estimated based on statistical regression. Therefore, the observable response indicators (X') can be calculated as follows:

$$X' = \frac{log(Y)-B}{A} \qquad (13)$$

The observable response indicators have the same policy implication as that of PR or FR, but they can be directly calculated from the baseline concentrations of certain chemical species rather than being derived from multiple CTM simulations. Therefore, these indicators are considerably more efficient than are traditional RSM-based indicators.

3. Results

3.1. Evaluating observable indicator performance in predicting chemistry regimes

3.1.1. O_3

Observable indicators and the PR are compared in Fig. 4, and the performance of observable indicators in predicting O_3 chemistry is summarized in Table 2. In general, strong correlation was noted between the observable indicators and PR. The indicator with the highest annual success rate was H_2O_2/HNO_3 approximately 73.4 %, with a value of 0.2 for the transition from NO_x-saturated to NO_x-

limited conditions. However, the original transition value of 0.2 for H_2O_2/HNO_3 tended to be too low, particularly in April, July, and October (see Fig. 4a). This study found that the annual success rate of H_2O_2/HNO_3 could be increased to 80.5 % if 0.3 was used as the transition value. This finding was consistent with corresponding findings in previous studies, which have suggested the transition values of H_2O_2/HNO_3 within the range of 0.2-3.6 at different locations and in different seasons (Sillman, 1995; Sillman et al, 1997; Lu and Chang, 1998; Tonnesen and Dennis, 2000; Hammer et al, 2002; Liang et al, 2006; Zhang et al., 2009). $H_2O_2/(O_3+NO_2)$, with a transition value of 0.02, also exhibited a high annual success rate of 66.4 %; this rate could be increased to 71.1 % by applying a transition value of 0.005 because the original transition value was too high, particularly in January, April, and October (see Fig. 4b). $HCHO/NO_y$ and $HCHO/NO_2$ exhibited relatively low performance, particularly in April and July, because the original transition values appeared to be too high (Fig. 4h and i). However, the performance of $HCHO/NO_y$ and $HCHO/NO_2$ could be greatly improved by using lower transition values, with increased annual success rates as high as 76 %. The change of the transition values implies that such indicators cannot fully consider all factors that determine the O_3 chemistry by using concentrations of just two species. The transition values of the indicators NO_y, O_3/NO_x, O_3/NO_y, and O_3/NO_z were suitable for estimating annual levels if only one unique transition value was applied for all months (apparently, these transition values for O_3/NO_x, O_3/NO_y and O_3/NO_z in January, and NO_x in April and July may have been too low). However, their success rates (all < 70 %) were not as high as those of other indicators. The inferior performance of the three O_3-involved indicators (O_3/NO_x, O_3/NO_y and O_3/NO_z) may have been associated with the considerable effects of background O_3, which cannot be removed easily.

Because $H_2O_2/(O_3+NO_2)$ and $HCHO/NO_2$ exhibited good performance in predicting O_3 chemistry, this study proposed a new indicator combining these two indicators, namely $H_2O_2 \times HCHO/NO_2$, with a transition value of 0.3. The results suggested that this new indicator has the highest annual success rate,

namely 87.3 %, among all the indicators. Studies (Sillman, 1995; Tonnesen and Dennis, 2000) have suggested that HCHO is approximately proportional to the VOC reactivity (i.e., the weighted sum of the reactions of VOCs with OH) and that HCHO/NO_2 closely approximates the competition between OH reactions with VOC and NO_2 that is central to O_3 chemistry. H_2O_2 derives from a key radical termination pathway under low NO_x conditions ($HO_2 + HO_2 \rightarrow H_2O_2 + O_2$). Comparison of H_2O_2 with NO_y or HNO_3, which derives from a key radical termination pathway under high NO_x conditions, $OH + NO_2 \rightarrow HNO_3$) represents the relative abundance of VOCs to NO_x. The new hybrid indicator incorporates information from the two individual indicators and could potentially be more robust.

3.1.2 $PM_{2.5}$

We selected the GR and AdjGR as observable indicators for $PM_{2.5}$ chemistry to identify NH_3-poor or NH_3-rich conditions. Comparison of GR and AdjGR with the FR is detailed in Fig. 5. AdjGR performance was much higher than that of the GR, with a larger annual success rate of 74.1 % compared with the GR's 55.6 % (see Table 3). The transition value of the GR appeared to be too low in all months (Fig. 5a). This result was consistent with those of previous studies; the AdjGR tends to be a more robust indicator because in contrast to the GR, it does not require an assumption of full sulfate neutralization (Zhang et al., 2009). The improvement of AdjGR compared to GR is the greatest in January and the smallest in July (Table 3). This is consistent with Pinder et al. (2008) who showed that accounting for DSN is important under cold temperatures but GR and AdjGR converge for higher temperatures.

This study designed a new indicator, total ammonia ratio (TAR), where the sulfate concentration is involved in the calculation, as follows:

$$TAR = \frac{[TA]^2}{[TN]\times[TS]} = \frac{[NH_3]\times[NH_4^+]}{([HNO_3]+[NO_3^-])\times[SO_4^{2-}]}, \qquad (14)$$

where $[TN]$ and $[TS]$ are the total molar concentrations of nitrate ($[HNO_3] + [NO_3^-]$) and sulfate

336 ($[SO_4^{2-}]$), respectively, and TAR is the relative abundance of total ammonia to nitrate and sulfate, regarded
337 as the product of $[TA]/[TN]$ and $[TA]/[TS]$. To simplify the calculation, $[TA]^2$ is assumed to be the
338 product of the molar concentration of ammonia gas $[NH_3]$ and ammonium $[NH_4^+]$.

339 The performance of TAR in predicting $PM_{2.5}$ chemistry was slightly higher than that of AdjGR, as
340 demonstrated by the higher success rate of TAR than that of AdjGR in all months. The annual success rate
341 of TAR was 79.6 %, with a transition value of 10 (Table 3).

342 **3.2 Developing the observable responsive indicators**

343 **3.2.1 O_3**

344 Fig. 6 presents the log-linear regressions of the O_3 observable indicators on the PR indicator derived
345 from the RSM. In general, all observable indicators exhibited strong correlations with the PR (all except
346 NO_y presented positive correlations with the PR), with varying R^2 values (0.08 – 0.75). The indicators
347 including NO_y, O_3/NO_x, O_3/NO_y, and O_3/NO_z, which had relatively low success rates, exhibited weaker
348 correlation with the PR ($R^2 < 0.31$; Fig. 6c-f). The newly developed $H_2O_2 \times HCHO/NO_2$ indicator exhibited
349 the strongest correlation with the PR ($R^2 = 0.75$), implying that the log-linear combination of the H_2O_2,
350 HCHO, and NO_2 baseline concentrations could approximate the responsive PR indicator to quantify O_3
351 chemistry. Other indicators can also be used to approximately estimate the PR based on the regression
352 coefficients shown in Fig. 6; however, their correlations with the PR were not as strong as those with
353 $H_2O_2 \times HCHO/NO_2$.

354 To evaluate the ability of the observable PR (oPR; estimated based on $H_2O_2 \times HCHO/NO_2$) to
355 represent the spatial and temporal variation of O_3 chemistry, the spatial distribution of the PR and oPR in
356 the four study months was compared across the simulated domain (Fig. 7). The oPR successfully captured
357 the strong NO_x-saturated regime in January ($PR < 1$) and the NO_x-limited ($PR > 1$) regime in July.

In addition, the PR and oPR suggested a consistently strong NO_x-saturated regime in northern and eastern China and key regions such as the YRD and PRD. The domain-averaged oPRs were 0.97, 1.52, 1.73, and 1.37 in January, April, July, and October, respectively; these values are similar to the PRs (0.77, 1.24, 1.38, and 1.17, respectively). Thus, the oPR may approximate the PR to quantify the O_3 chemistry, even on a large spatial and temporal scale.

3.2.2. $PM_{2.5}$

The correlations between $PM_{2.5}$ observable indicators and the responsive FR indicator derived from the RSM were investigated (Fig. 8). The AdjGR has the lowest R^2 (0.40) because of its high variations for the NH_3-poor condition (Fig. 5b). A stronger positive correlation was noted between the GR and FR (R^2 = 0.57); however, the success rate of the GR was the lowest among all the indicators (the success rate of the GR increased when the transition value was set as the median value of the GR, namely 5, at an FR of 1). The TAR exhibited the strongest positive correlation with the FR (R^2 = 0.60), implying that the FR can be approximately estimated by the log-linear combination of baseline concentrations of ammonia gas, nitric acid gas, particulate ammonium, sulfate, and nitrate.

The capability of the observable FR (oFR; estimated based on the TAR indicator) in representing the spatial and temporal variation of $PM_{2.5}$ chemistry is illustrated in Fig. 9. Both the FR and oFR suggested strong NH_3-poor condition (FR > 1) in January and NH_3-rich condition (FR < 1) in April and July. The oFR suggested strong NH_3-rich condition in northern and eastern China and the Sichuan Basin; these findings were consistent with those for the FR. The domain-averaged oFRs were 1.56, 1.05, 0.86, and 1.24 in January, April, July, and October, respectively, with the strongest NH_3-poor condition in January and NH_3-rich condition in July. These findings were comparable with the FRs of 1.47, 1.16, 0.95, and 1.19 for the four study months, respectively, suggesting that the oFR can approximate the FR to quantify the $PM_{2.5}$ chemistry and its spatial and temporal variations.

3.3. Policy implications

3.3.1. O_3

The responsive PR indicator may help policy-makers to understand the status and extent of O_3 chemistry in the current scenarios. A lower PR (< 1) suggested a NO_x-saturated regime. Moreover, the VNr could be used to inform policy-makers about the level of simultaneous control of VOCs required to prevent an increase in O_3 levels from NO_x controls. In general, the VNr is negatively correlated with the PR because a lower PR implies a stronger NO_x-saturated regime, which in turn requires more simultaneous VOC control with NO_x. By contrast, a higher PR implies a weaker NO_x-saturated or even NO_x-limited regime, which requires less or no simultaneous control of VOCs with NO_x. The negative correlation between VNr and the PR was quantified by the simple linear regression of VNr on PR (Fig. S7). A high R^2 (approximately 0.82) suggested that the VNr originally derived from the RSM can also be approximately estimated from the PR or oPR.

Figure 10 presents a comparison of the VNr derived from the RSM, with the VNr calculated based on the oPR, estimated by the $H_2O_2 \times HCHO/NO_2$ indicator and denoted as oVNr. Consistent spatial and temporal variations were found for VNr and oVNr. Additional simultaneous VOC control is required in January and in northern and eastern China, and is highly correlated with the low PR (Fig. 7). The domain-averaged oVNr values were estimated to be 0.95, 0.43, 0.38, and 0.47 in January, April, July, and October, respectively, with the highest and lowest oVNr values noted in January and July, respectively. That is comparable with VNr in the four study months (i.e., 0.82, 0.46, 0.34, and 0.57, respectively).

The annual-averaged VNr and PR were also calculated for each province in China (Fig. 11). VNr was negatively correlated with the PR at the provincial level. The northern provinces, namely Heilongjiang, Xinjiang, and Liaoning required the highest VNr (1-1.2) because their PRs were very low (0.3-0.4). In the NCP, including the province of Tianjin, Hebei, Henan, Shandong, Shanxi, Inner Mongolia, and Beijing,

high VNr (0.7-0.9) was required to overcome the stronger NO_x-saturated regime (PR = 0.4-0.6). The coastal provinces, namely Fujian, and Guangdong, and middle-eastern provinces, namely Jiangxi and Hunan, also demonstrated relatively high PRs (>0.7) and low VNr (<0.3).

3.3.2. $PM_{2.5}$

Using the responsive FR indicator or its observable oFR indicator can rapidly identify NH_3-rich or NH_3-poor conditions, and this information can aid policy-makers in estimating the additional $PM_{2.5}$ benefit associated with simultaneous control of NH_3 and NO_x emissions (ΔC_NH_3). As discussed in Section 2.2, ΔC_NH_3 can be calculated from the RSM using the first derivative of the $PM_{2.5}$ responsive function to NH_3. Therefore, ΔC_NH_3 must be strongly associated with the secondary inorganic aerosol (SNA) concentration, as suggested in Fig. S8, which demonstrates a strong correlation between SNA concentration and ΔC_NH_3. The linear regression with high R^2 (>0.71) implies that the ΔC_NH_3 can be approximately calculated based on the SNA concentration.

The ΔC_NH_3 estimated based on the SNA concentration ($o\Delta C\_NH_3$; based on the regression function in Fig. S8) was compared with that derived from the RSM (Fig. 12). The $o\Delta C\_NH_3$ typically captured the spatial and temporal variation of ΔC_NH_3, suggesting large benefits in January and October, particularly in eastern China and the Sichuan Basin. The domain-averaged ΔC_NH_3 values were approximately 0.31, 0.22, 0.16, and 0.38 μg m^{-3} $PM_{2.5}$ per 10 % NH_3 reduction in January, April, July, and October respectively. In April and July, $o\Delta C\_NH_3$ presented consistent results approximately 0.21 and 0.16 μg m^{-3} $PM_{2.5}$, respectively, per 10 % NH_3 reduction, but slightly underestimated the benefits in January and October (0.24 and 0.22 μg m^{-3} $PM_{2.5}$, respectively, per 10 % NH_3 reduction).

At the annual level, ΔC_NH_3 was compared with the population-weighted $PM_{2.5}$ concentration in each province (Fig. 13). ΔC_NH_3 ranged from 2 to 12 μg m^{-3} $PM_{2.5}$ per 10 % NH_3 reduction. In addition, the provinces with higher $PM_{2.5}$ exposure exhibited additional benefits from NH_3 reductions (i.e., high

427 ΔC_NH_3), particularly in Hunan, Shandong, Tianjin, Jiangxi, Anhui, Henan, and Hubei where ΔC_NH_3
428 was > 8 μg m^{-3} $PM_{2.5}$ per 10 % NH_3 reduction. These benefits from simultaneous NH_3 control were
429 substantial enough to be considered in these regions for achieving the national ambient $PM_{2.5}$ target (35
430 μg m^{-3}).

431 **3.3.3. Cobenefits of NO_x and VOC control in reducing O_3 and $PM_{2.5}$**

432 NO_x and VOCs are major precursors for O_3 and $PM_{2.5}$, and effectively controlling their emissions
433 can lead to cobenefits in reducing O_3 and $PM_{2.5}$. The PR results suggest strong NO_x-saturated regimes in
434 northern and eastern China including key regions such as the Sichuan Basin, YRD, and PRD, where
435 simultaneous VOC control with a certain VOC-to-NO_x ratio is required to prevent increases in O_3 levels
436 from the NO_x controls. $PM_{2.5}$ senstivity to NO_x can be negative under a strong NO_x-saturated regime; this
437 effect is not as significant as it is for O_3 (Fig. 3). We quantified the nonlinearity of $PM_{2.5}$ sensitivity to NO_x
438 by using the same PR concept but for $PM_{2.5}$ response (Text S2); Fig. S9 presents the spatial distribution
439 of the PR to identify $PM_{2.5}$ sensitivity to NO_x emission in the four study months. The PR values for $PM_{2.5}$
440 were > 1 in April, July, and October in all grid cells across China, suggesting that NO_x control is always
441 beneficial for $PM_{2.5}$ reduction during these months. Even in January, the PR for $PM_{2.5}$ (0.4-0.8 in eastern
442 and northern China) remains larger than that for O_3 (0.2-0.6 in eastern and northern China), implying that
443 the suggested VNr for O_3 was high enough to overcome the potential limitations on $PM_{2.5}$ reduction from
444 NO_x control.

445 To explore the cobenefits of reducing O_3 and $PM_{2.5}$ after simultaneous control of NO_x and VOCs,
446 we investigated the effectiveness of six control pathways with various VOC-to-NO_x ratios including 0,
447 0.2, 0.4, 0.6, 0.8 and 1.0 (Fig. 14). In general, O_3 and $PM_{2.5}$ concentrations can be reduced in all months
448 through simultaneous control of NO_x and VOC emissions, although different VNr and control levels are
449 required in different months. In January (under strongly NO_x-saturated conditions), reductions in $PM_{2.5}$

and O_3 require VOC emission controls in addition to NOx controls to prevent potential disbenefits associated with the nonlinear chemistry. The smaller VNr required for $PM_{2.5}$ (~0.4) than for O_3 (~1.0) in this case might be associated with the smaller PR for $PM_{2.5}$ as well as the additional benefit of VOC controls in reducing secondary organic aerosols. Apparently, a larger VNr control ratio and greater emission control is required in January compared with other months. In Fig. 14(a), only one pathway can achieve simultaneous reduction in O_3 and $PM_{2.5}$ concentrations (i.e., the pathway with VNr equal to 1 and at the far end of the pathway, with reduction rates > 80%). In April and October, simultaneous VOC controls were still required for O_3 (VNr = 0.2-0.6) but not for $PM_{2.5}$. In July when NO_x-limited regime was dominant, the NO_x control was critical because the VOC controls had little effect on either O_3 or $PM_{2.5}$. At the annual level, the simultaneous VOC controls (40 % of the NO_x controls) led to cobenefits in reducing both O_3 and $PM_{2.5}$ at the national level. However, VNr varied significantly in different seasons, suggesting that considering the seasonality of O_3 and $PM_{2.5}$ chemistry is necessary for design of a season-specific control strategy.

4. Summary and conclusion

Compared with conducting multiple CTM simulations, the indicator method proved more efficient in identifying the chemical regime in the current scenarios. However, the traditional indicators are not as useful as the RSM-based PR and FR indicators for policy-makers to infer feasible emission reduction paths. Therefore, this study quantified the relationship between RSM-based and traditional-observable indicators and developed new observable response indicators, the oPR and oFR, which can be used to quantify the nonlinearity of O_3 and $PM_{2.5}$ response to precursor emissions. Similar to the traditional indicators, the oPR and oFR can be easily calculated using a combination of ambient concentrations of certain chemical species obtained from surface-monitored observations, modeling simulations, or even satellite retrievals. In addition, the observable responsive indicators can not only rapidly identify the

chemical regime but also provide policy-makers with useful information, such as simultaneous VOC controls to prevent increases in O_3 levels from NO_x controls under the NO_x-saturated regime (i.e., VNr), as well as the additional benefit of simultaneously reducing NH_3 alongside NO_x control in $PM_{2.5}$ reductions (i.e., ΔC_NH_3). Since the indicators are developed from simulations with spatially uniform emission controls across the country, they are especially useful for providing quick estimates of the potential benefits or risks from uniform controls. These estimates can also provide a basis to design more localized control strategies for particular regions.

This study proposed a new O_3-chemistry indicator, namely $H_2O_2 \times HCHO/NO_2$, and $PM_{2.5}$-chemistry indicator, namely the TAR, both of which exhibited the highest success rates among all the indicators. This study also suggested that the log-linear combinations of baseline H_2O_2, HCHO, and NO_2 concentrations could provide an approximate PR to quantify O_3 chemistry spatially and temporally. Similarly, the log-linear combination of baseline concentrations of ammonia gas, nitric acid gas, particulate ammonium, sulfate and nitrate can be used to approximately estimate the FR for $PM_{2.5}$ chemistry. The VNr was highly correlated with the PR, suggesting that a stronger NO_x-saturated regime requires greater VOC control accompanied by NO_x control. The positive correlation between ΔC_NH_3 and the population-weighted $PM_{2.5}$ concentration suggested that a province with high $PM_{2.5}$ exposure can gain greater benefits from NH_3 reduction. Finally, simultaneous control of NO_x and VOC could reduce both O_3 and $PM_{2.5}$ throughout the year, and an effective control pathway (VNr = 0.4) could lead to the cobenefits of reducing both O_3 and $PM_{2.5}$. However, VNr varied significantly among the seasons and provinces, suggesting the necessity of considering the seasonality of chemistry and of designing a more localized control strategy for each province. We note that the discrepency between the observable indicator and the responsive indicator might also be influcenced by uncertainties in the chemical mechanism of CMAQ as well as prediction errors of the pf-RSM. The new indicators were designed based on the existing

chemical mechanism, and the transition values might be refined in the future as our understanding of atmospheric chemical processes improves.

In conclusion, the two unique aspects of this study are as follows. First, quantification of the correlation of observable indicators with responsive indicators (Fig. 5 and 7) implied that the traditional observable indicators, based on monitored or satellite-retrieved concentrations, can be used to quantify the nonlinearity of $PM_{2.5}$ and O_3 to precursor emission and provide useful policy implications. Second, this study reported a promising method for efficiently establishing $PM_{2.5}$- and O_3- responsive functions to precursors for traditional responsive or reduced-form modeling studies. This study suggested that the PR or FR (a combination of coefficients in the polynomial functions in the pf-RSM) can be approximately estimated using the ambient concentration of certain chemical species. Similarly, all coefficients in polynomial functions can be calculated based on a set of ambient concentrations of certain chemical species. The simple log-linear regression method used in this study demonstrated the possibility that even in the presence of uncertainties in prediction, more advanced data analytics technologies such as deep learning may improve performance in future.

Data availability

The pf-RSM outputs and code package are available upon request from the corresponding author.

Author contribution

These authors contributed equally to this work: Jia Xing & Dian Ding. JX designed the methodology and wrote the paper. DD conducted the modeling experiment and analyzed the data. SW provided ideas and financial support and edited the paper. ZD and YZ helped with the modeling experiment. JK, CJ and JH provided ideas and edited the paper.

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682 **Table 1.** Terms in the pf-RSM design for O_3 and $PM_{2.5}$

Term	O_3	$PM_{2.5}$
1	NO_x^5	VOC
2	NO_x^4	NH_3
3	NO_x^3	NH_3^2
4	NO_x^2	NH_3^3
5	NO_x	SO_2
6	VOC	VOC^2
7	VOC^2	NO_xVOC
8	VOC^3	NO_x^2VOC
9	NO_xVOC	NO_x^4VOC
10	NO_xVOC^3	NO_xNH_3
11	NO_x^5VOC	NO_x
12	NO_x^2VOC	NO_x^2
13	SO_2	NO_x^3
14	NH_3	NO_x^4

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686 **Table 2.** Summary of observable indicators and their performances in predicting O_3 chemistry

Indicator		success rate at TV (%)						success rate at TV' (%)				
	TV*	Jan	Apr	Jul	Oct	ANN	TV'	Jan	Apr	Jul	Oct	ANN
H_2O_2/HNO_3	0.2	68.8	74.9	89.0	60.8	73.4	**0.3**	77.9	83.0	90.4	70.6	80.5
$H_2O_2/(O_3+NO_2)$	0.02	81.1	41.9	85.4	57.4	66.4	**0.005**	69.2	73.3	88.8	53.3	71.1
NO_y	5	38.9	47.8	87.8	40.9	53.8	-	-	-	-	-	-
O_3/NO_x	15	56.5	75.8	58.8	71.7	65.7	-	-	-	-	-	-
O_3/NO_y	7	60.7	65.8	23.3	68.2	54.5	-	-	-	-	-	-
O_3/NO_z	7	43.5	75.0	76.4	67.0	65.5	-	-	-	-	-	-
$HCHO/NO_y$	0.28	83.9	32.5	19.4	50.9	46.7	**0.1**	66.7	77.7	86.3	75.6	76.6
$HCHO/NO_2$	1	87.3	49.7	27.4	73.8	59.6	**0.5**	75.7	77.2	69.1	82.2	76.1
$H_2O_2 \times HCHO/NO_2$	-	-	-	-	-	-	**0.3**	92.3	81.6	89.5	86.0	87.3

687 * TV- transition value as summaried in Zhang et al (2009); TV' - transition value proposed in this study

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691 **Table 3.** Summary of observable indicators and their performances in predicting $PM_{2.5}$ chemistry

Indicator		success rate (%)				
	TV	Jan	Apr	Jul	Oct	ANN
Gas ratio (GR)	1*	51.7	59.3	69.6	41.7	55.6
Adjusted Gas ratio (AdjGR)	1*	81.8	73.3	74.0	67.5	74.1
Total Ammonia Ratio (TAR)	10**	86.2	77.5	80.6	74.0	79.6

692 * TV- transition value as proposed in Zhang et al (2009);

693 ** TV- transition value as proposed in this study

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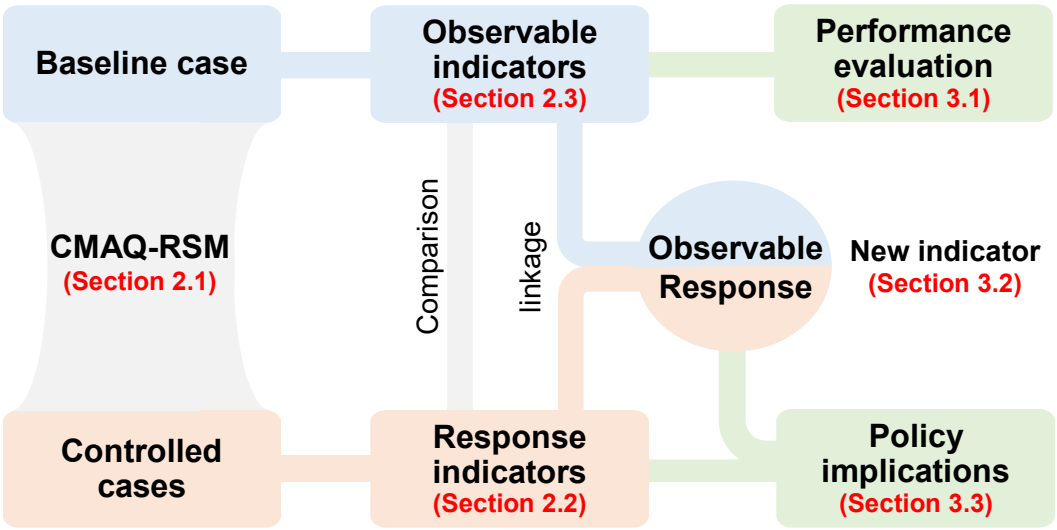


Figure 1. Flow of observable response indicator development and application

Figure 2. Simulation domain over mainland China (27 × 27-km^2 resolution, 182 × 232 grid cells). The 31 provinces are BJ-Beijing; TJ-Tianjin; HEB- Hebei; SX-Shanxi; IM-Inner Mongolia; LN- Liaoning; JL- Jilin; HLJ-Helongjiang; SH- Shanghai; JS-Jiangsu; ZJ-Zhejiang; AH- Anhui; FJ- Fujian; JX-Jiangxi; SD- Shandong; HEN- Henan; HUB-Hubei; HUN- Hunan; GD-Guangdong; GX- Guangxi; HN-Hainan; CQ- Chongqing; SC- Sichuan; GZ-Guizhou; YN- Yunnan; TB- Tibet; SHX-Shaanxi; GS-Gansu; QH-Qinghai; NX- Ningxia; and XJ-Xinjiang)

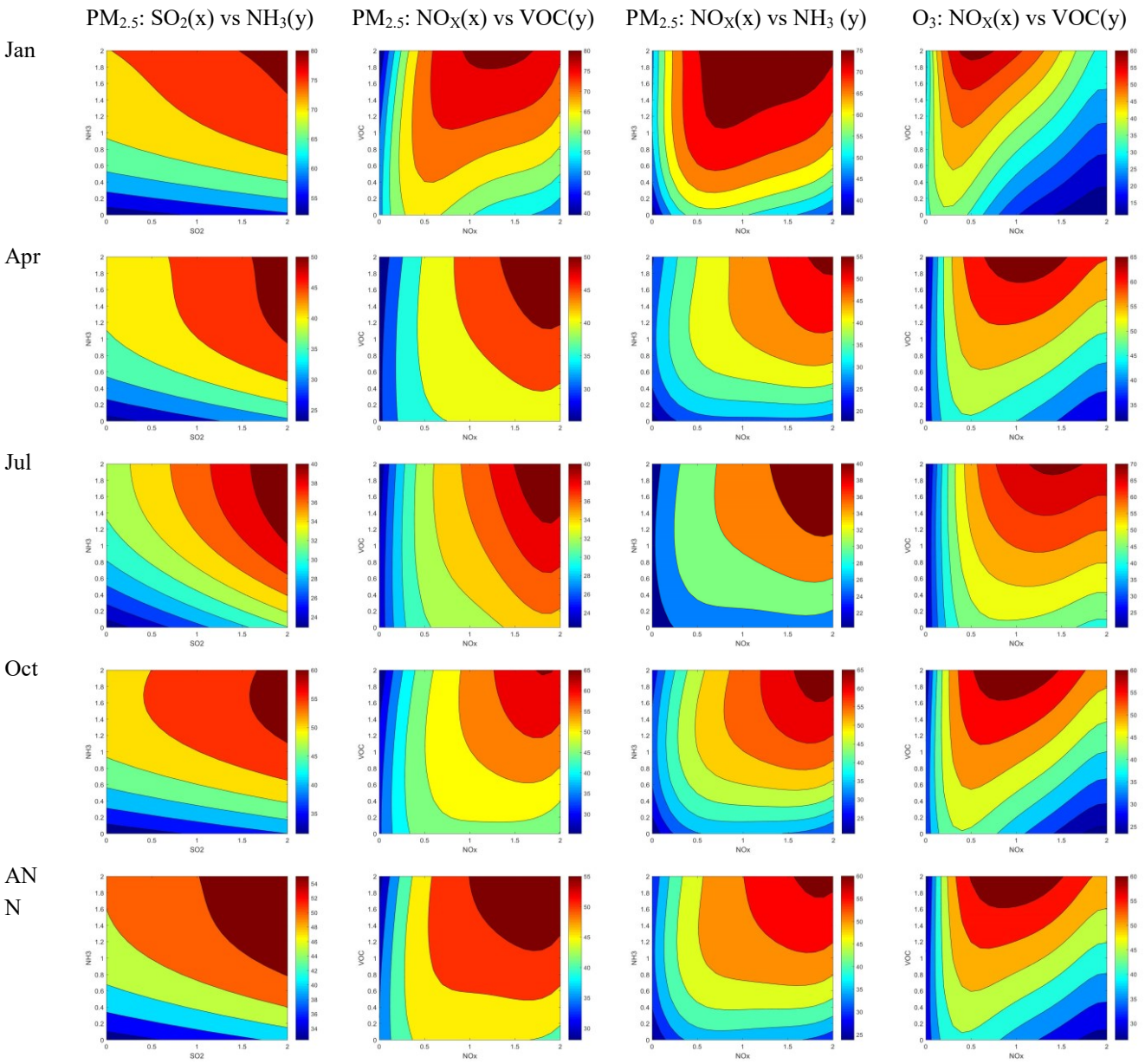
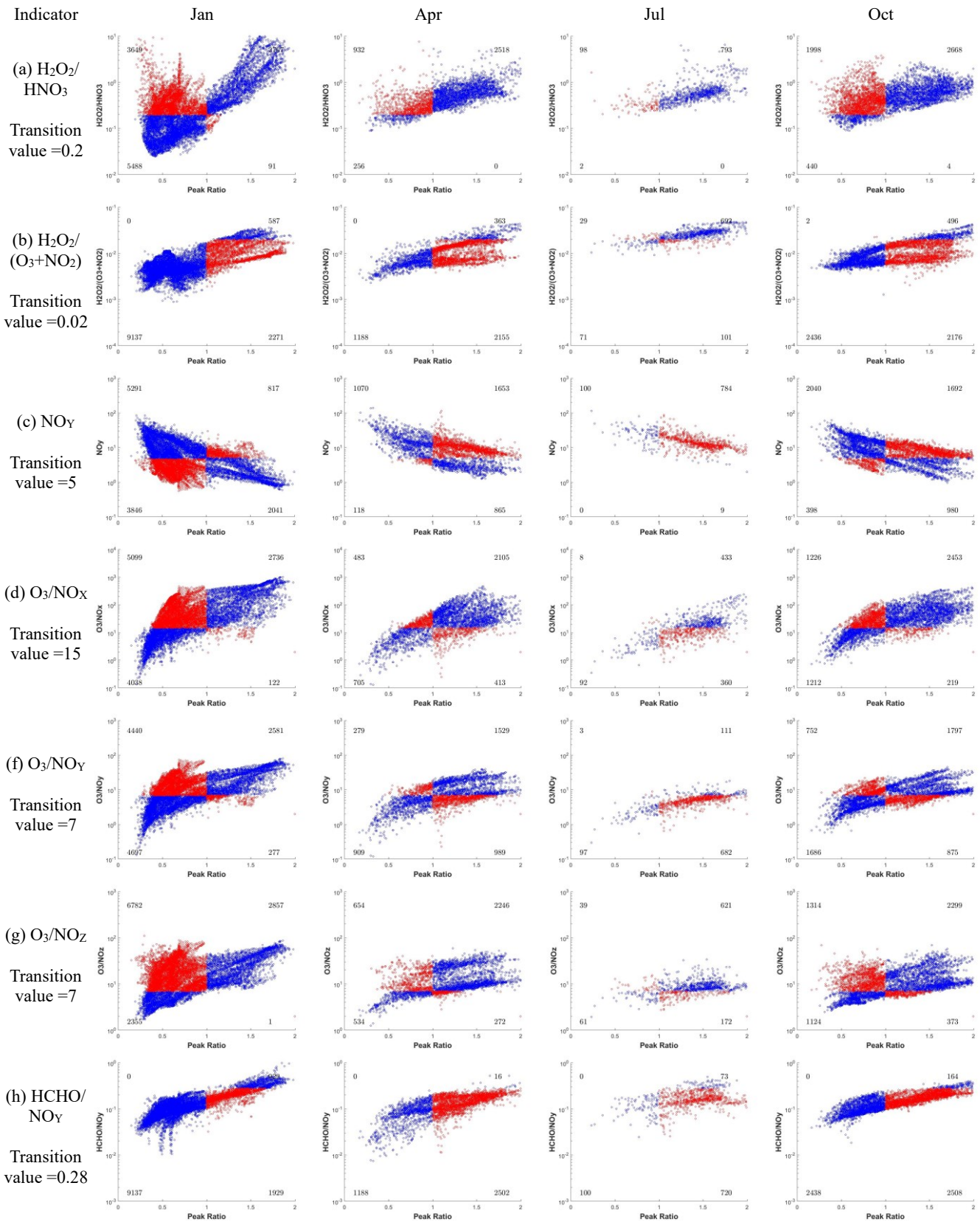


Figure 3. Isopleth of population-weighted $PM_{2.5}$ and daytime O_3 to precursor emission change in different months. (The x- and y- axes represent precursor emission rates with a baseline of 1, applied to all grid cells in China; background colors represent the population-weighted $PM_{2.5}$ and daytime O_3 concentrations in China, with units of μg m^{-3} for $PM_{2.5}$ and ppb for O_3)


Indicator
Jan
Apr
Jul
Oct
(a) H2O2/HNO3
Transition value =0.2
(b) H2O2/(O3+NO2)
Transition value =0.02
(c) NOY
Transition value =5
(d) O3/NOX
Transition value =15
(f) O3/NOY
Transition value =7
(g) O3/NOZ
Transition value =7
(h) HCHO/NOY
Transition value =0.28
Peak Ratio

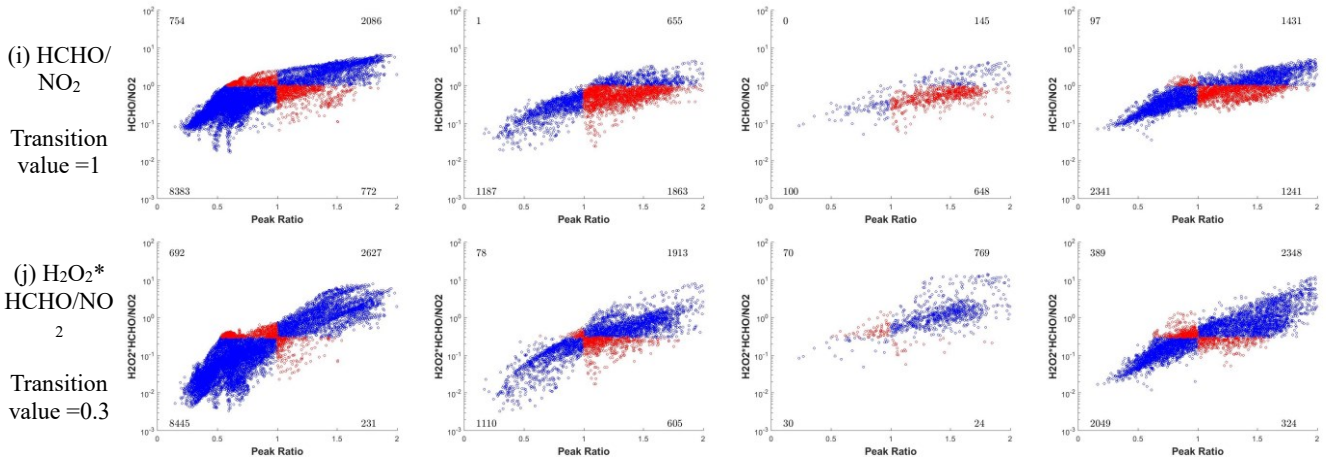
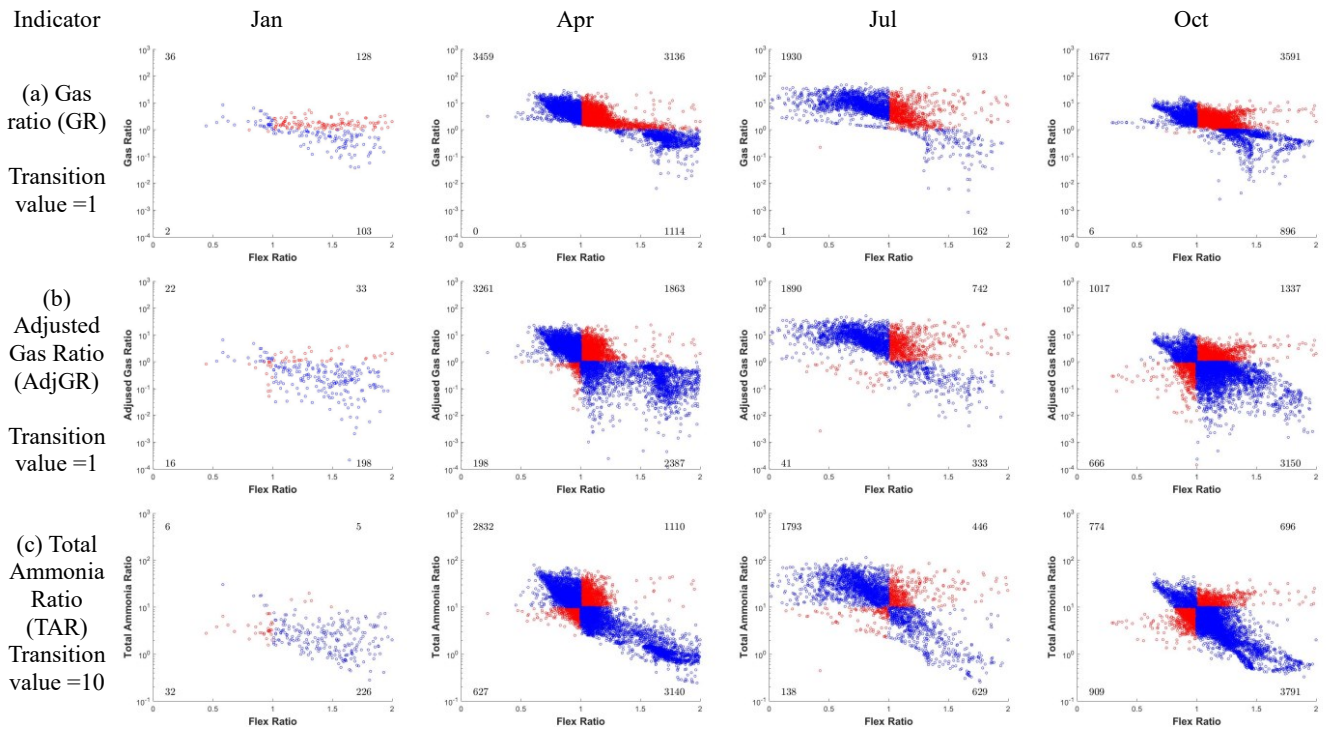


Figure 4. Performance of observable indicators in predicting O_3 chemistry. The x-axis represents the PR values where the transition value is 1, and the y-axis represents the observable indicators. The blue dots represent the grids where O_3 chemistry is successfully predicted by the observable indicator; the red dots represent the grids where the observable indicator fails to predict O_3 chemistry. The numbers in the four corners represent the grid number in each section; the number in July is much lower than those in the other months because most grids are located at the NO_x-limited regime with PR > 2 in July.



718 **Figure 5.** Performance of observable indicators in predicting $PM_{2.5}$ chemistry. The x-axis represents the
719 FR values where the transition value is 1, and the y-axis represents the observable indicators. The blue
720 dots represent the grids where $PM_{2.5}$ chemistry is successfully predicted by the observable indicator; the
721 red dots represent the grids where the observable indicator fails to predict $PM_{2.5}$ chemistry. The numbers
722 in the four corners represent the grid number in each section; the number in January is much lower than
723 those in the other months because most grids are located at the NH_3-poor condition with FR>2 in
724 January.

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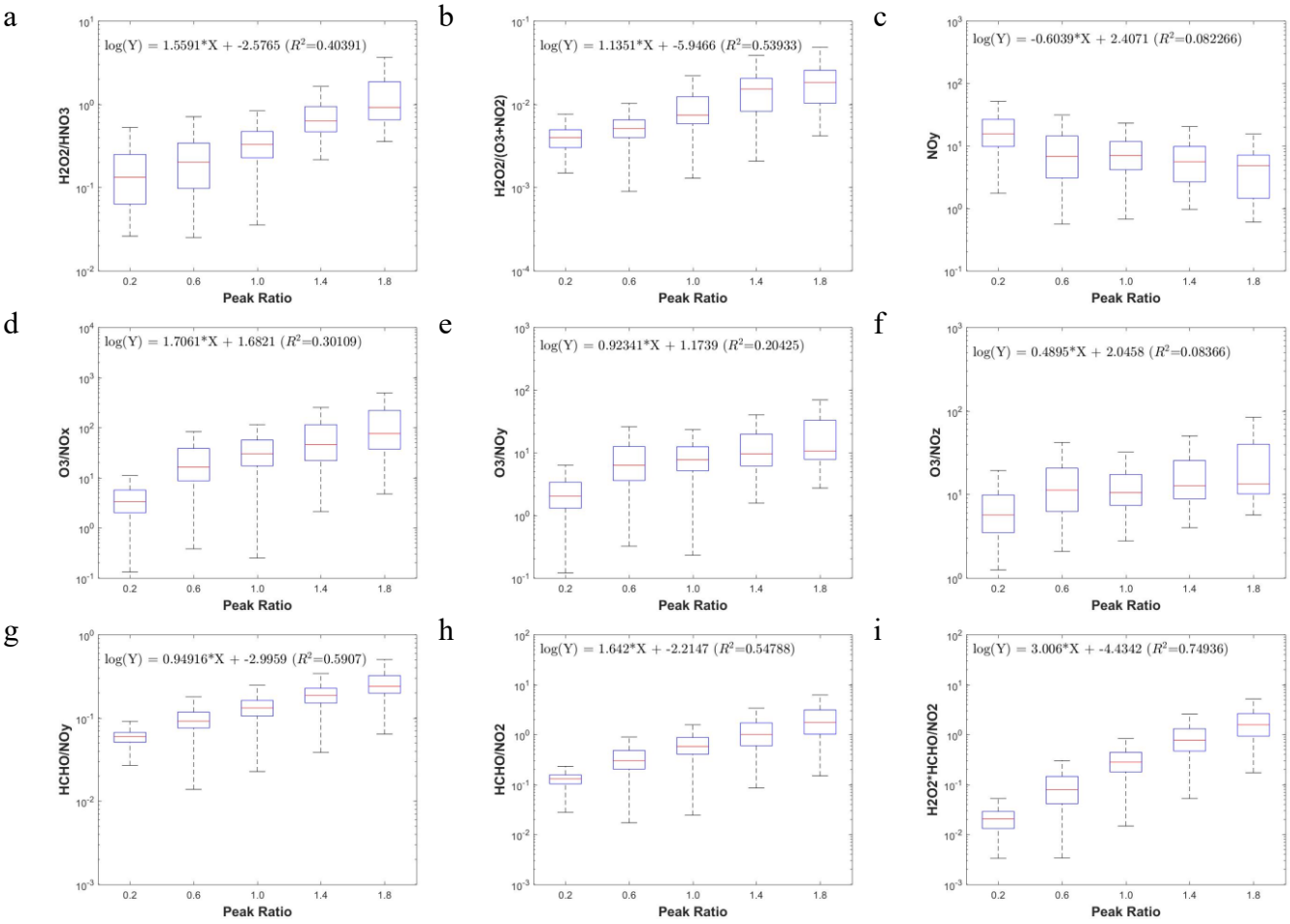
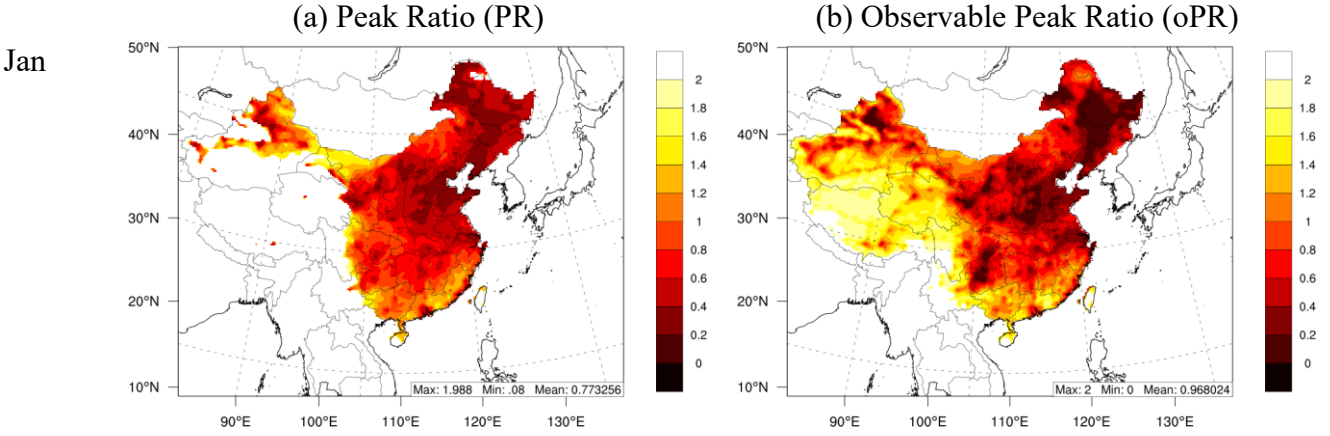
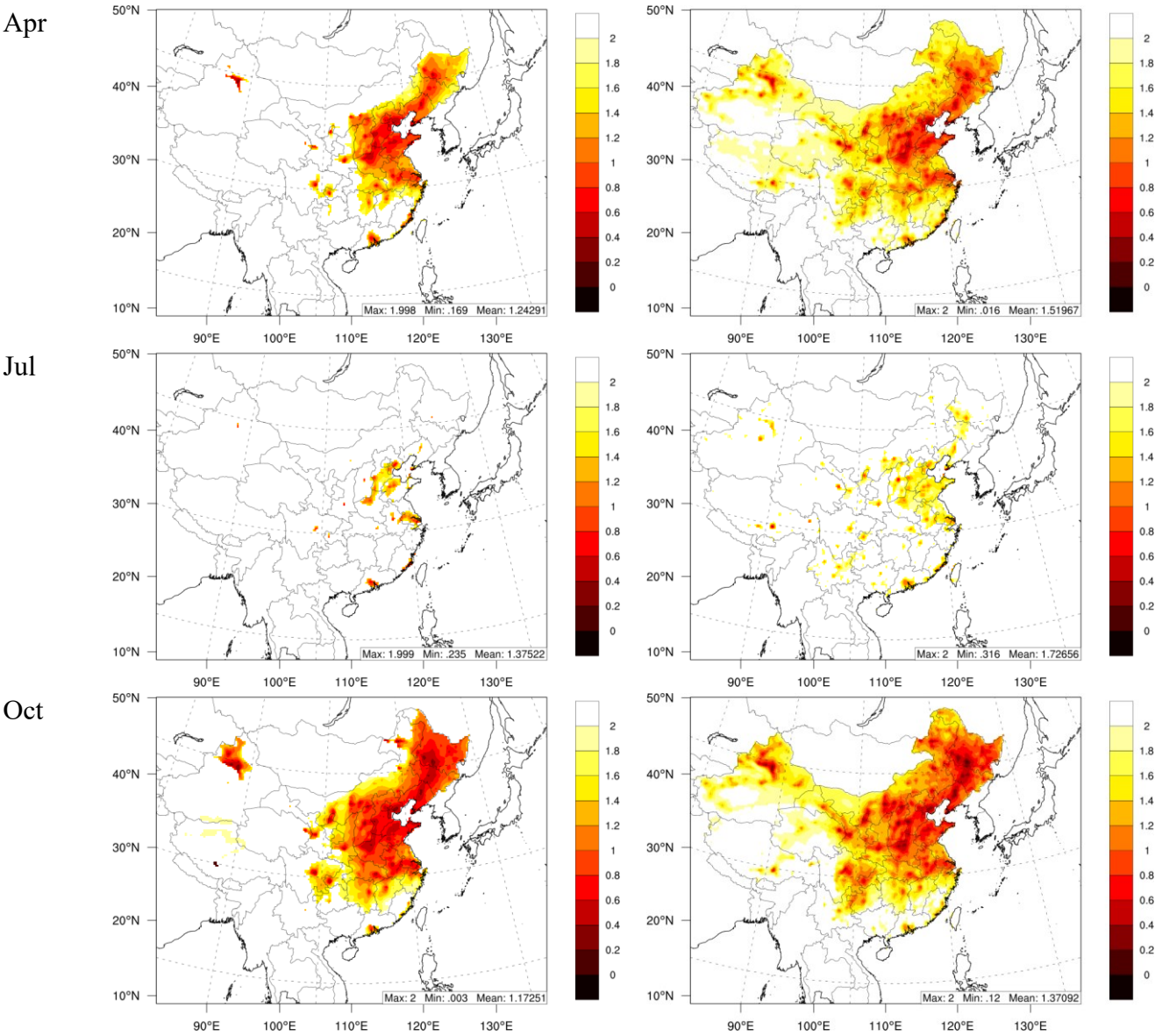
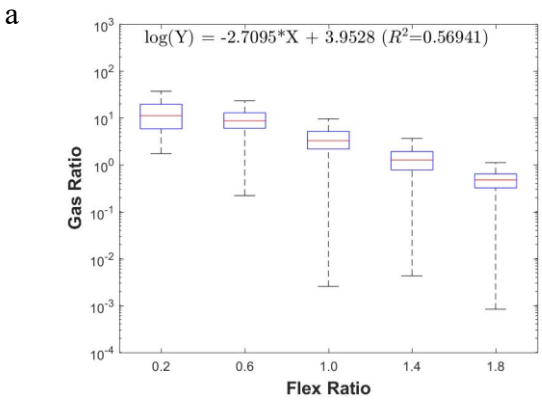


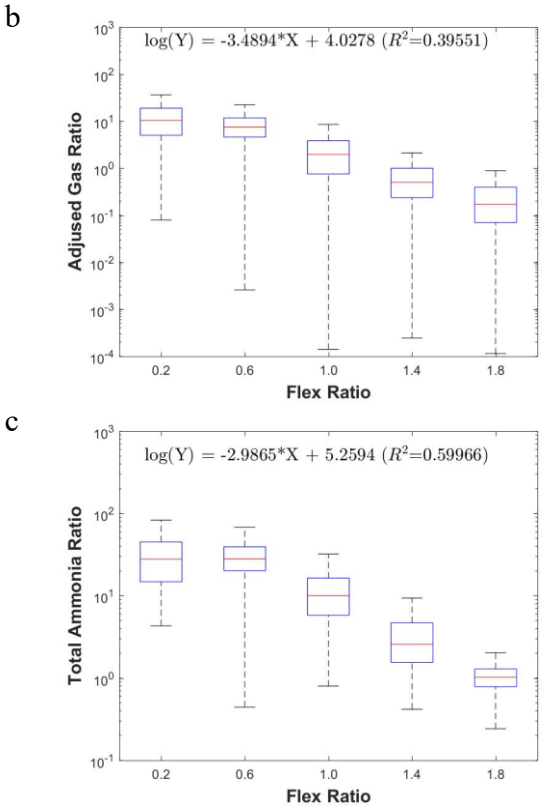
Figure 6. Development of observable responsive indicators for O_3 chemistry based on log-linear regressions between observable indicators and the PR.





728 **Figure 7.** Comparison of the PR derived from the RSM with that calculated from concentrations for O_3
729 chemistry. The oPR was estimated based on $H_2O_2 \times HCHO/NO_2$.





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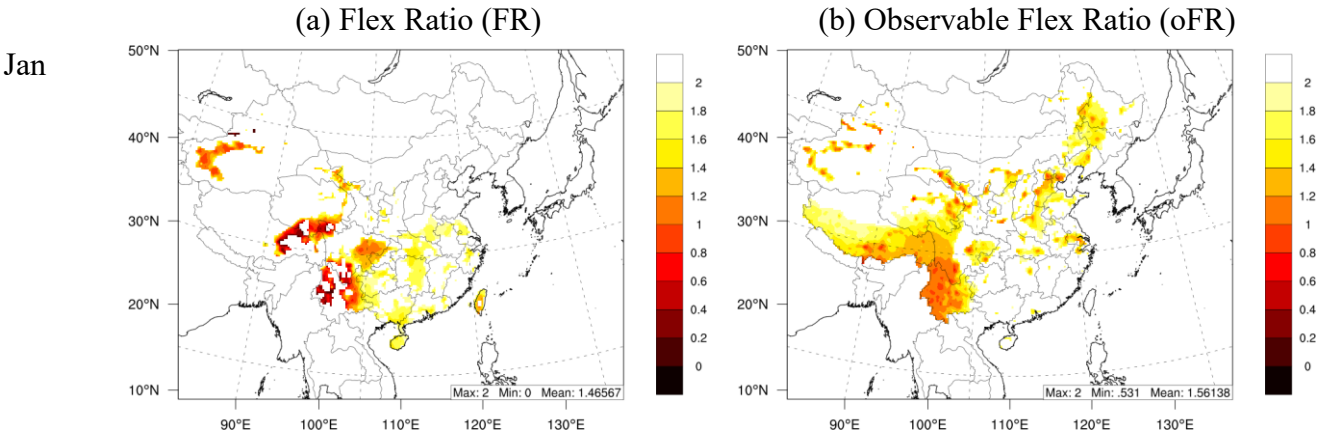
731 **Figure 8.** Development of observable responsive indicators for $PM_{2.5}$ chemistry based on log-linear
732 regressions between observable indicators and the FR



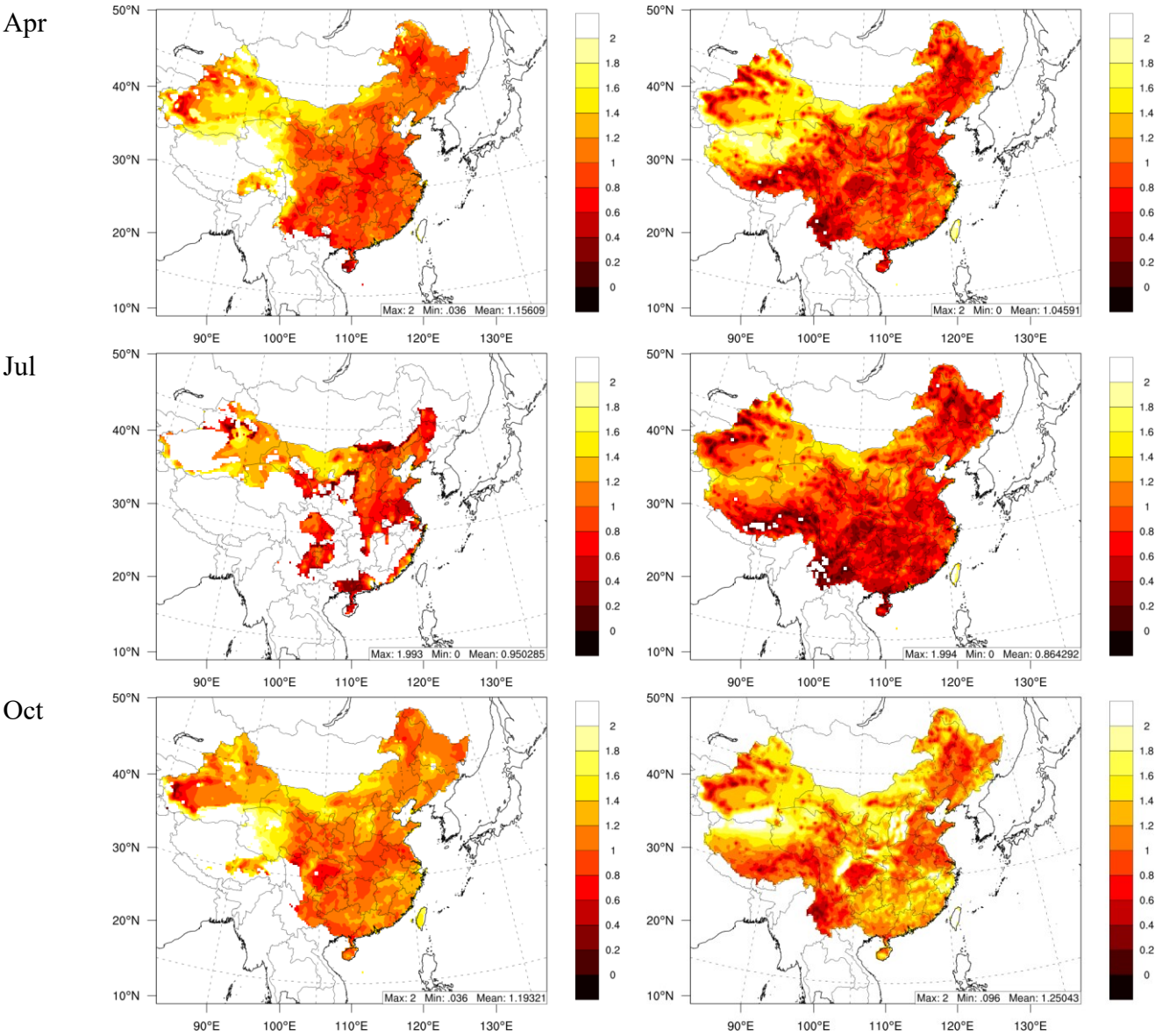


Figure 9. Comparison of the FR derived from the RSM with that calculated from concentrations for $PM_{2.5}$ chemistry. The oPR was estimated based on TAR.

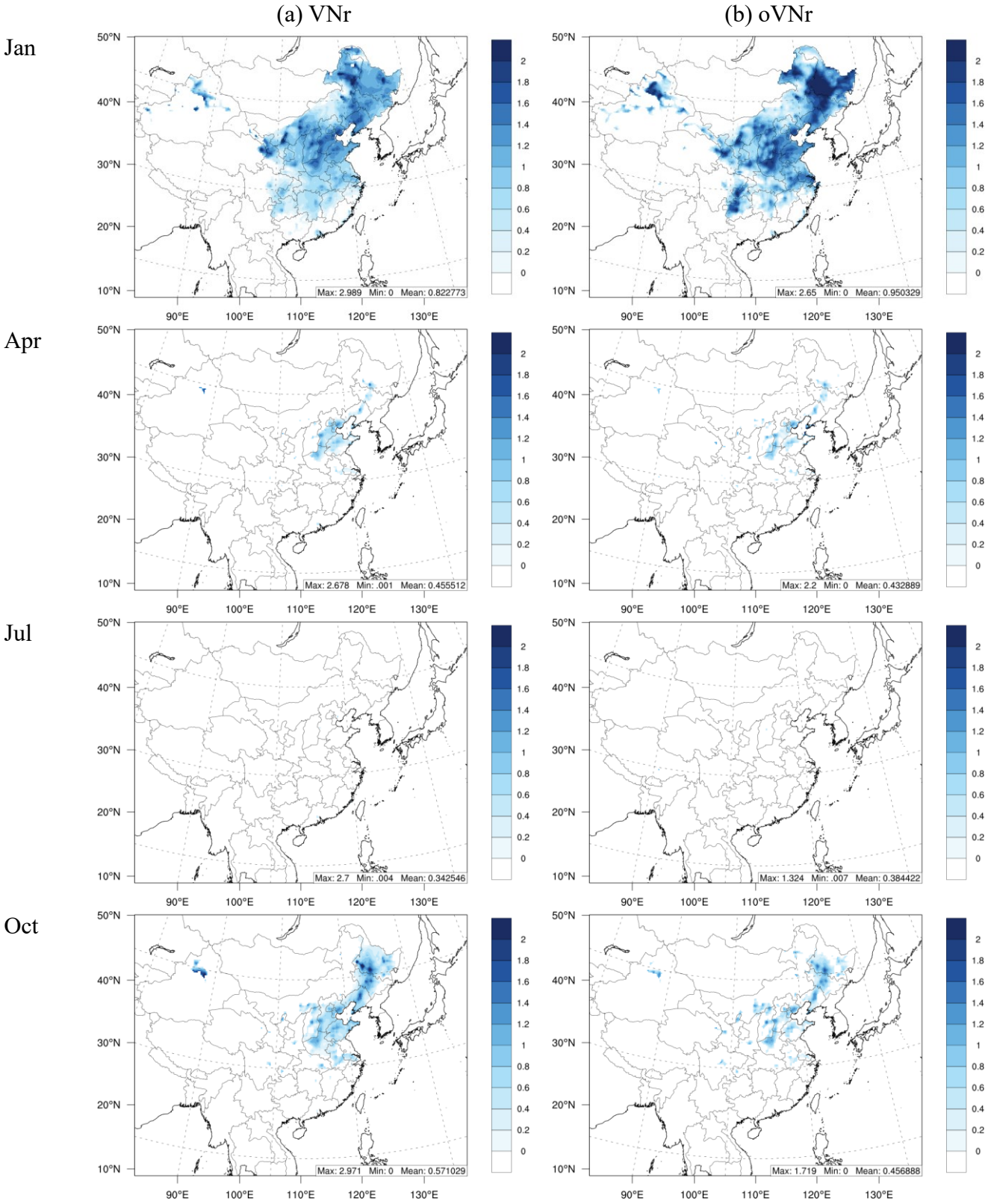


Figure 10. Comparison of VNr with oVNr.

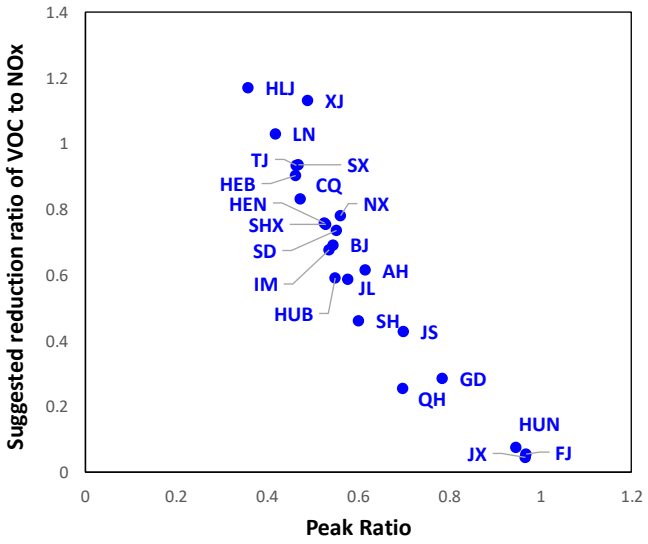


Figure 11. Comparison of the annual-averaged PR with VNr in each province in China

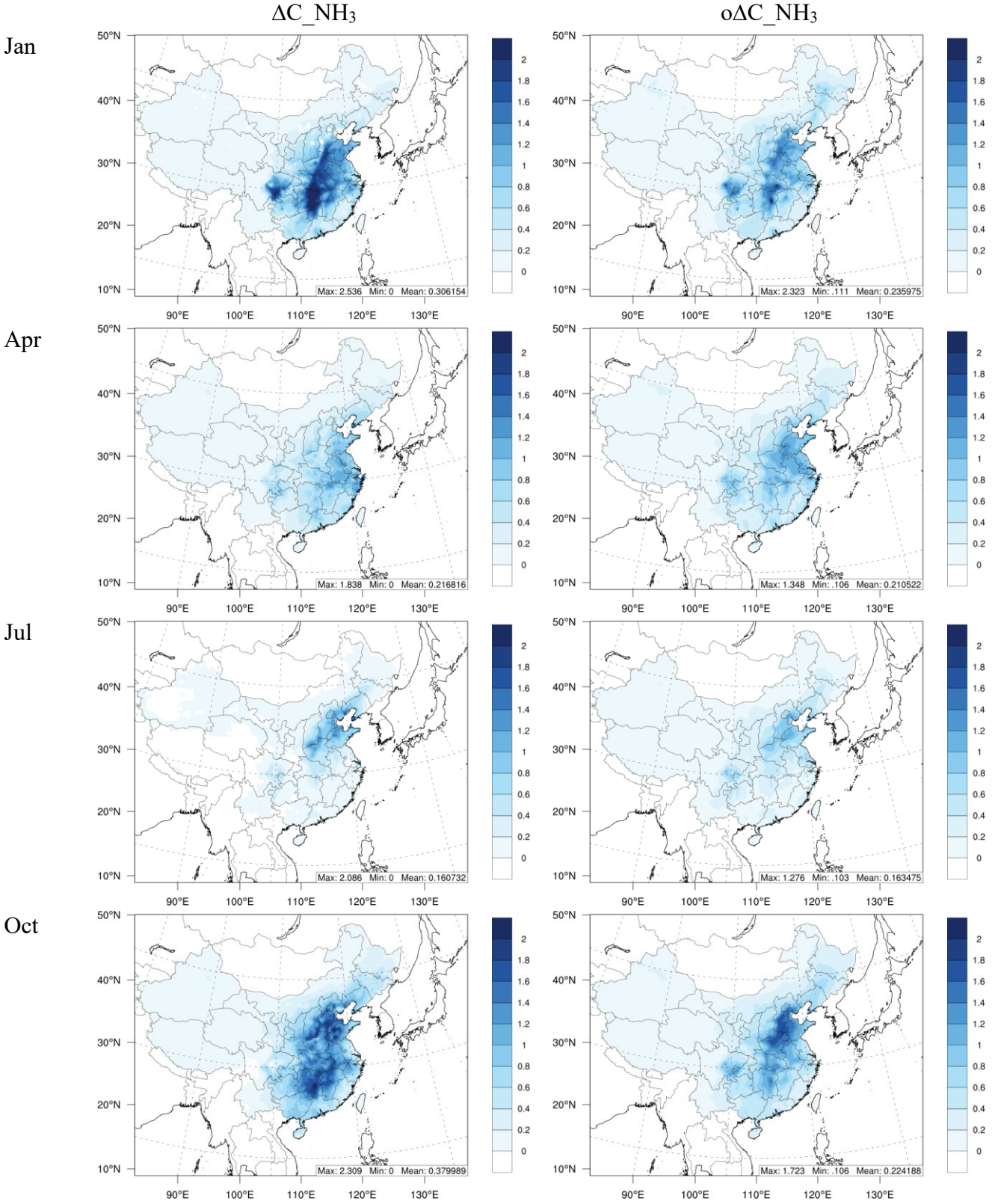


Figure 12. Comparion of the benefit in reducing $PM_{2.5}$ from simultaneous NH_3 reduction (ΔC_NH_3) with that calculated from concentrations ($o\Delta C\_NH_3$)

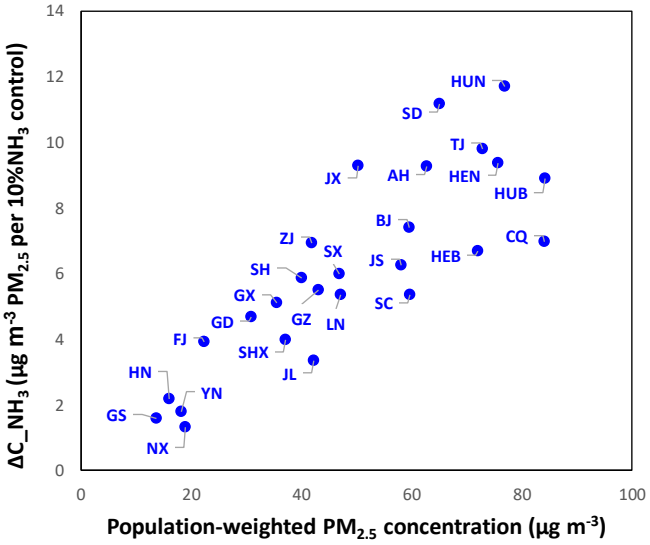


Figure 13. Comparison of annual-averaged benefit in reducing $PM_{2.5}$ from simultaneous NH_3 reduction (ΔC_NH_3) and population-weighted $PM_{2.5}$ concentration in each province in China

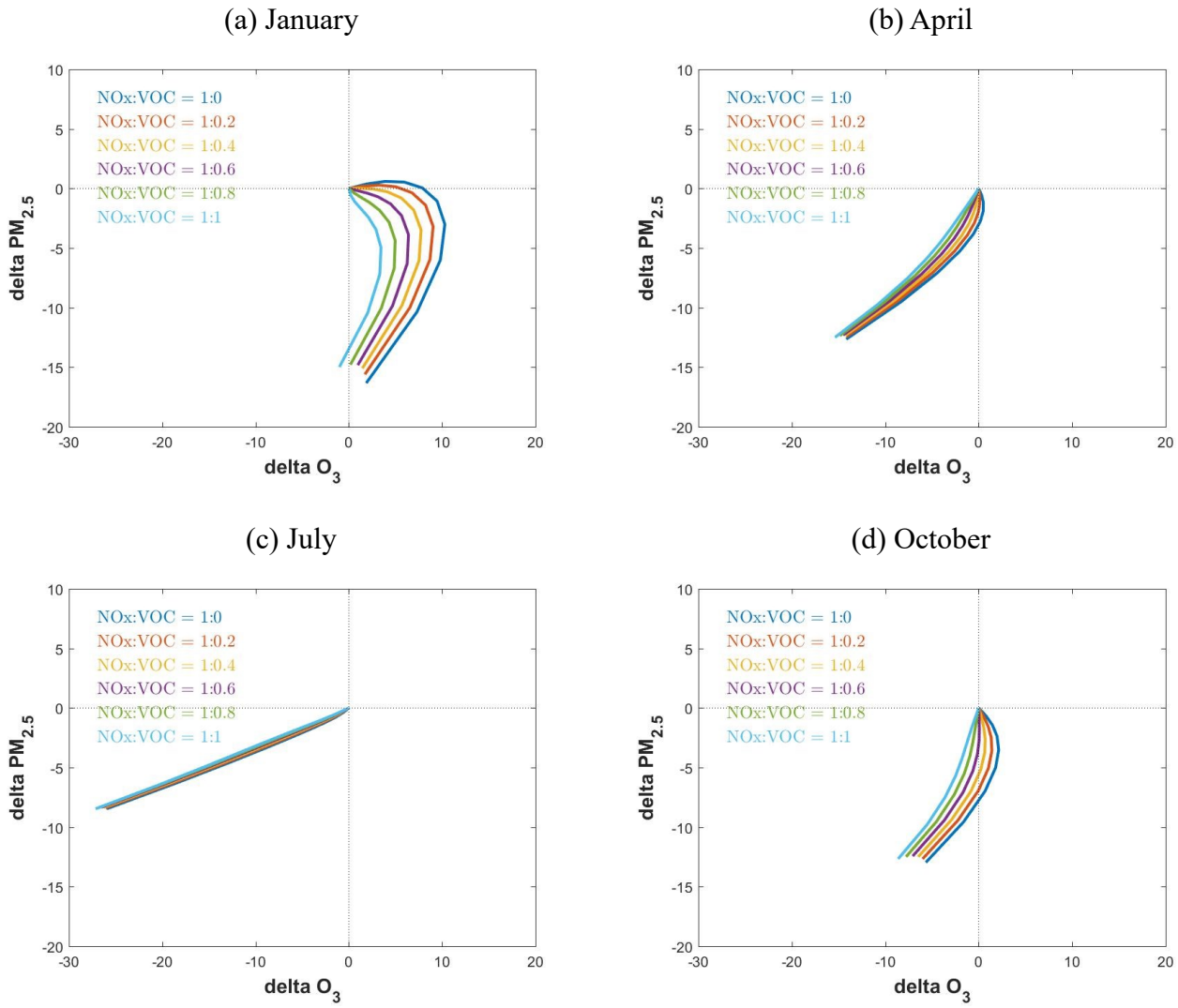


Figure 14. Control effectiveness with different NO_x and VOC ratios in reducing population-weighted $PM_{2.5}$ and O_3 concentrations (in $\mu g\ m^{-3}$) in China (NO_x is from no control to 80 % reduction)