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

Designing effective control policies requires efficient quantification of the nonlinear response of air 17 pollution to emissions. However, neither the current observable indicators nor the current indicators based 18 19 on response-surface modeling (RSM) can fulfill this requirement. Therefore, this study developed new 20 observable RSM-based indicators and applied them to ambient fine particle (PM_{2.5}) and ozone (O₃) 21 pollution control in China. The performance of these observable indicators in predicting O₃ and PM_{2.5} chemistry was compared with that of the current RSM-based indicators. H₂O₂×HCHO/NO₂ and total 22 23 ammonia ratio, which exhibited the best performance among indicators, were proposed as new observable 24 O₃- 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 25 can serve as an indicator to approximately quantify the response of O₃ and PM_{2.5} to changes in precursor 26

27 emissions. The observable RSM-based indicator for O₃ (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-28 saturated regime in northern and eastern China and their key regions, including the Yangtze River Delta 29 and Pearl River Delta. The observable RSM-based indicator for PM_{2.5} (observable flex ratio) also captured 30 strong NH₃-poor condition in January and NH₃-rich condition in April and July, as well as NH₃-rich in 31 northern and eastern China and the Sichuan Basin. Moreover, analysis of these newly developed 32 observable response indicators suggested that the simultaneous control of NH₃ and NO_x emissions 33 produces greater benefits in provinces with higher $PM_{2.5}$ exposure by up to 12 µg m⁻³ $PM_{2.5}$ per 10 % NH₃ 34 reduction compared with NOx control only. Control of volatile organic compound (VOC) emissions by as 35 much as 40 % of NO_x controls is necessary to obtain the co-benefits of reducing both O₃ and PM_{2.5} 36 exposure at the national level when controlling NO_x emissions. However, the VOC-to-NO_x ratio required 37 to maintain benefits varies significantly from 0 to 1.2 in different provinces, suggesting that a more 38 localized control strategy should be designed for each province. 39

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

43 **1. Introduction**

Air pollution has attracted great attention because of its harmful effects on human health (Cohen et 44 al., 2017), climate (Myhre et al., 2013), agriculture and ecosystems (Fuhrer et al., 2016), and visibility 45 (Friedlander et al., 1977). In particular, ambient fine particles ($PM_{2.5}$) and ozone (O_3) are among the top 46 risk factors for global mortality (Forouzanfar et al., 2015; Cohen et al., 2017) and have increased the need 47 to effectively control anthropogenic sources in order to reduce the ambient concentrations of PM2.5 and 48 O₃ (Wang et al., 2017). The challenge is that the dominant contributions to ambient PM_{2.5} and O₃ arise 49 from a series of chemical reactions among precursors, including sulfur dioxide (SO₂), nitrogen oxides 50 (NO_x) , ammonia (NH_3) and volatile organic compounds (VOCs) (Seinfeld and Pandis, 2012). The 51 52 complexity of the chemical reactions and pathways associated with variations in meteorological conditions and precursor levels results in strong nonlinear responses of PM2.5 and O3 to their precursor 53 emission changes (West et al., 1999; Hakami et al., 2004; Cohan et la., 2005; Pun et al., 2007; Megaritis 54 55 et al., 2013). Such nonlinearity issues are a major challenge for policy-makers to design an effective 56 control strategy.

Chemical species in the atmosphere are often highly correlated with one another, since their 57 concentrations are affected by common atmospheric physical processes (e.g., mixing and transport) and 58 chemical reactions. Concentrations of pollutants such as O₃ and PM_{2.5} are typically determined based on 59 the ambient levels of their gaseous precursors, implying that O₃ and PM_{2.5} chemistry can be identified 60 through a combination of concentrations of some of their related chemical species (i.e., indicators). The 61 62 empirical kinetic modeling approach (EKMA) developed by the U.S. EPA quantifies the relationships of 63 O_3 with its precursor concentrations based on O_3 chemistry (Freas et al., 1978; Gipson et al., 1981). The 64 EKMA plot can aid inference of control strategy effectiveness (e.g., NO_x or VOC control) according to 65 VOC-to-NO_x ratios. Several studies have developed "observable" indicators by relating O₃ to reactive

nitrogen concentrations and species related to atmospheric oxidation. Such indicators include NO_v, 66 H₂O₂/HNO₃, HCHO/NO₂ and H₂O₂/(O₃+NO₂) (Milford et al., 1994; Sillman, 1995; Tonnesen and Dennis, 67 2000; Sillman and He, 2002), which can be used to identify NOx-saturated or -limited regimes. The O_3 68 indicators can be derived from surface-monitoring observations (Peng et al., 2006), modeling simulations 69 (Wang et al., 2010), or even satellite retrievals (Jin et al., 2017; Sun et al., 2018), and then examined using 70 71 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 72 73 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 NH₃-poor or -rich conditions 74 (Ansari and Pandis, 1998; Takahama et al., 2004; Pinder et al., 2008; Dennis et al., 2008). The indicator-75 76 based method can be efficient in determining the chemical regime in the current scenarios and in qualitatively estimating O₃ and PM_{2.5} sensitivities to small perturbations in precursor emissions or ambient 77 concentrations without involving complex CTMs. However, traditional indicator methods are unable to 78 79 quantify the extent of the chemistry regime (Pinder et al., 2008); hence, the traditional observable 80 indicators provide policy-makers limited information for reducing O₃ and PM_{2.5} pollution.

The sensitivity of O_3 and $PM_{2.5}$ to precursor emissions can be explored by running multiple brute-81 force CTM simulations. For instance, the response surface model (RSM) developed from brute-force 82 simulations can generate a wide range of O_3 and $PM_{2.5}$ responses to precursor emissions ranging from 83 fully controlled to doubled emissions (i.e., -100 % to 100 % change relative to the baseline emission) 84 (Xing et al., 2011; Wang et al., 2011). Based on the RSM, the chemical response indicators of Peak Ratio 85 (PR) and Flex Ratio (FR) have been designed to identify regimes of O₃ and PM_{2.5} chemistry, respectively 86 87 (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 88

converts to another regime. With the recent development of the polynomial function-based RSM (pf-90 RSM), the PR and FR can be easily calculated (Xing et al., 2018). However, this method is built on at 91 least 20 CTM simulations; in other words, the estimating the PR and FR requires considerable computing 92 resources. As a result, RSM use remains limited despite recent improvements in RSM efficiency (Xing et 93 al., 2017).

94 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 95 PM_{2.5} exposure (Zhao et al., 2018; Ding et al., 2019a). However, during this period, significant increases 96 97 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 98 27 %, 19 %, and 8 % in the North China Plain (NCP), Yangtze River Delta (YRD), and Pearl River Delta 99 (PRD), respectively (Ding et al., 2019b). Greater control over anthropogenic sources must be enforced to 100 reduce PM_{2.5} and O₃ concentrations (Lu et al., 2018). Notably, accurate quantification of the nonlinear 101 responses of O₃ and PM_{2.5} to their precursor emissions is critical and a prerequisite for effective mitigation 102 of air pollution in China. 103

The design of an effective O₃ and PM_{2.5} control strategy requires efficient quantification of air 104 105 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 106 chemical species. It is expected that the response indicators originally derived from RSM predictions (i.e., 107 108 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 109 110 numerous CTM simulations. To support the needs of policy design for O₃ and PM_{2.5} control, this study 111 developed effective indicators that not only represent O₃ 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.

120 **2. Method**

121 **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 122 simulate the baseline concentrations of O₃ and PM_{2.5} and their responses in numerous emission control 123 124 scenarios with different emission change ratios. The simulation was conducted on a domain covering China with 27 km \times 27 km horizontal resolution (Fig. 2). In 2017, January, April, July, and October were 125 simulated to represent winter, spring, summer, and fall, respectively. An annual level was estimated as the 126 average of the levels in these four months. The concentration data was analyzed based on the monthly 127 average for afternoon O₃ (12:00–18:00 China Standard Time when O₃ was the highest across a day), and 128 monthly average for 24-h PM_{2.5}. To approximate exposure concentrations, we also estimated population-129 weighted O₃ and PM_{2.5} at the regional or national level by averaging the gridded concentrations weighted 130 by the population in each grid cell. The gridded population data were obtained from the 1 km \times 1 km 131 132 LandScan population dataset in 2016 (Oak Ridge National Laboratory, 2013).

133 The anthropogenic emission data were developed by Tsinghua University by using a bottom-up 134 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 135 reports. The anthropogenic emissions were gridded into 27 km × 27 km horizontal resolution to match the 136 CMAQ model (Fig. S1). The 2017 biogenic emissions over China were generated using the Model for 137 Emissions of Gases and Aerosols from Nature (MEGAN; version 2.04). The meteorology field, driven by 138 the Weather Research and Forecasting Model (WRF; version 3.7), followed the same configuration as that 139 140 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-141 surface physics scheme, and the ACM2 PBL physics scheme. We used NCEP FNL (Final) Operational 142 143 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 144 simulating wind speed, humidity and temperature (Table S1). The CMAQ model performance in 145 reproducing O₃ and PM_{2.5} concentrations was evaluated by comparison with the ground-based 146 observations (Fig. S2), which suggested acceptable CMAQ model performance that met the recommended 147 benchmark (Ding et al., 2019a,b). The normalized mean biases of CMAQ in predicting PM_{2.5} and O₃ are 148 -16.4% and -12.5% compared with monitoring data obtained from the China National Environmental 149 Monitoring Centre. The mean fractional biases for $PM_{2.5}$ and O_3 prediction are -14.2% and -11.1%, 150 151 respectively (within the benchmark of $\pm 60\%$). The mean fractional errors for PM_{2.5} and O₃ prediction are 21.6% and 17.0% respectively (within the benchmark of 75%). The RSM was developed based on multiple 152 CTM simulations for various emission-control scenarios according to the brute-force method. Identical to 153 154 our previous RSM studies (Xing et al., 2017, 2018), the responses of O₃ and PM_{2.5} to precursor emissions were analyzed using the baseline case and 40 control scenarios using the Latin Hypercube Sample method 155 156 for four control variables, namely the emission ratios of NO_x, SO₂, NH₃, and VOCs. Though the responses 157 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 162 163 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 164 $PM_{2.5}$ and O_3 responses has been evaluated in detail using leave-one-out cross validation as well as the 165 166 out-of-sample validation method, with normalized errors all within 5% for both PM2.5 and O3 across the domain. Relatively large biases occurred for marginal cases, where emissions are controlled by nearly 167 100% and predicted concentrations are very small. These cases have limited influence on the shape of 168 nonlinear curve of the response function. However, the RSM is developed from a suite of CMAQ 169 simulations, and so uncertainties in the chemical mechanism used in CMAQ might influence the O3 and 170 171 PM_{2.5} predictions.

172 2.2. RSM-based indicators of O₃ and PM_{2.5} chemistry

Based on the developed pf-RSM, the nonlinear responses of O₃ and PM_{2.5} concentrations to precursor emissions can be represented as follows:

175
$$\Delta Conc = \sum_{i=1}^{n} X_i \cdot (\Delta E_{NOx})^{a_i} \cdot (\Delta E_{SO2})^{b_i} \cdot (\Delta E_{NH3})^{c_i} \cdot (\Delta E_{VOCs})^{d_i}$$
(1)

where $\Delta Conc$ is the change in O₃ 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, SO₂, NH₃, and VOC emissions (i.e., $\Delta Emissions / Baseline_Emissions$), 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 14 181 (*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 187 for annual-averaged population-weighted O₃ and PM_{2.5} concentrations in 31 provinces in China are 188 provided in Table S3 and Table S4, respectively. The terms with first degree for NOx, SO₂, NH₃, and 189 VOCs represent the first derivative of PM_{2.5} and O₃ response to each precursor emission. O₃ was more 190 191 sensitive to NO_x (term X_5) and VOCs (term X_6) than to SO₂ (term X_{13}) or NH₃ (term X_{14}), and O₃ sensitivity was negative to NO_x but positive to VOCs in most provinces. PM_{2.5} sensitivities to the four 192 precursors (terms X1, X2, X5 and X11 for VOCs, NH3, SO2, and NOx, respectively) were comparable, 193 194 whereas $PM_{2.5}$ sensitivity to NO_x could be negative or positive.

The nonlinearities of O₃ and PM_{2.5} to precursors were mainly determined by high-order and 195 196 interaction terms. To illustrate such nonlinearities further, we used a series of isopleths, as shown in Fig. 197 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 198 as $PM_{2.5}$ and O_3 responses to NO_x and VOCs in different months. Strong nonlinearity was noted in $PM_{2.5}$ 199 sensitivity to NH₃, and in O₃ and PM_{2.5} sensitivities to NO_x. PM_{2.5} sensitivity to NH₃ increased alongside 200 the transition of $PM_{2.5}$ chemistry from the NH₃-rich condition (typically at high NH₃ emission ratios) to 201 the NH₃-poor condition (typically at low NH₃ emission ratios). O₃ 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 202 203 under the NO_x-limited regime (typically at low NO_x emission ratios). In addition, the transition points (corresponding to the NO_x or NH₃ ratios at which the chemical regime for O₃ 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 NH₃-poor condition appears in winter because of low NH₃ evaporation and little agriculture activity which is a dominant NH₃ 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 O₃ and FR for PM_{2.5}) were calculated as described in our previous studies (Xing et al., 2011, 2018; Wang et al., 2011).

For O₃, the PR can be directly calculated as follows:

213
$$PR = 1 + \Delta E_{NOx} |_{\frac{\partial \Delta Conc_{O3}}{\partial \Delta E_{NOx}} = 0} E_{NOx} \epsilon[a, b] \qquad (2)$$

214 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:

215
$$5 * X_1 * \Delta E_{NOx}^4 + 4 * X_2 * \Delta E_{NOx}^3 + 3 * X_3 * \Delta E_{NOx}^2 + 2 * X_4 * \Delta E_{NOx} + X_5 = 0 \quad (3)$$

The PR is the NO_x emissions (represented as $1 + \Delta E_{NOx}$) that produce maximum O₃ 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 O₃ 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:

221
$$VNr = r |_{\frac{\partial \Delta Conc_{O3}}{\partial \Delta E_{NOx}} = 0} \quad when PR < 1 \quad , r = \frac{\Delta E_{VOC}}{\Delta E_{NOx}} / \Delta E_{NOx} \quad (4)$$

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}

223 and ΔE_{NH3} are 0, $\frac{\partial \Delta Conc_{O3}}{\partial \Delta E_{NOx}}$ can be written as follows:

224
$$5 * X_1 * \Delta E_{NOx}^4 + 4 * X_2 * \Delta E_{NOx}^3 + 3 * X_3 * \Delta E_{NOx}^2 + 2 * X_4 * \Delta E_{NOx} + X_5 + X_6 * r + 2 * X_7 * C_{NOx}^2 + 2 * X_4 * \Delta E_{NOx}^2 + 2 * X_6 * r + 2 * X_7 * C_{NOx}^2 + 2 * X_8 + 2 * X_8$$

225
$$r^2 * \Delta E_{NOx} + 3 * X_8 * r^3 * \Delta E_{NOx}^2 + 2 * X_9 * r * \Delta E_{NOx}^2 + 4 * X_{10} * r^3 * \Delta E_{NOx}^3 + 6 * X_{11} * r * C_{NOx}^3 + 6 * X_{10} * C_{NOx}^3 + C_{NOx}^3 + C_{NOx}^3 + C_{NOx}^3 + C_{NOx}^3 +$$

$$\Delta E_{NOx}^{5} + 3 * X_{12} * r * \Delta E_{NOx}^{2} = 0$$
 (5)

227 Since the ΔE_{NOx} is close to 0 when the controls are taken from the baseline, we ignore the terms of ΔE_{NOx} 228 in the first derivative function above, then it can be written as follows,

229
$$X_5 + X_6 * r = 0$$
 (6)

230 The VNr therefore can be calculated using the following equation:

$$VNr = -\frac{X_5}{X_6} \tag{7}$$

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 NH₃ 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 NH₃ emission ratio when the PM_{2.5} sensitivity to NH₃ 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):

238

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

239 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,

240 and ΔE_{NH3} can be obtained as follows:

241
$$3 * X_4 * \Delta E_{NH3}^2 + (2 * X_3 - X_{10}) * \Delta E_{NH3} + X_2 - X_{11} = 0$$
(9)

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

247
$$\Delta C_N H_3 = \left(\frac{\partial \Delta Conc_{PM2.5}}{\partial \Delta E_{NOx}}\Big|_{\Delta E_{NH3} = \Delta E_{NOx}}\right) - \left(\frac{\partial \Delta Conc_{PM2.5}}{\partial \Delta E_{NOx}}\Big|_{\Delta E_{NH3} = 0}\right)$$
(10)

248 where

249 $\frac{\partial \Delta Conc_{PM2.5}}{\partial \Delta E_{NOx}}|_{\Delta E_{NH3}=\Delta E_{NOx}}$ is the first derivative of the $\Delta Conc_{PM2.5}$ response to ΔE_{NOx} when $\Delta E_{NH3} =$

250 ΔE_{NOx} , and

251 $\frac{\partial \Delta Conc_{PM2.5}}{\partial E_{NOx}}|_{E_{NH3}=0}$ is the first derivative of the $\Delta Conc_{PM2.5}$ response to ΔE_{NOx} when $\Delta E_{NH3}=0$.

252 $\Delta C_N H_3$ can be calculated as follows:

$$\Delta C_N H_3 = X_2 \tag{11}$$

254 2.3. Observable indicators of O₃ and PM_{2.5} chemistry

Zhang et al. (2009) summarized the various observable indicators with their corresponding transition 255 values to identify O₃ and PM_{2.5} chemistry: O₃ indicators were H₂O₂/HNO₃, H₂O₂/(O₃+NO₂), NO_y, O₃/NO_x, 256 O₃/NO_y, O₃/NO_z, HCHO/NO_y, and HCHO/NO₂, and the PM_{2.5} indicators were the DSN, GR, and AdjGR 257 258 (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 259 260 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 261 Table 2. In the present study, we examined these transition values and compared their performance in 262 predicting O₃ and PM_{2.5} chemistry. Because the RSM-based indicators, PR and FR, are calculated using 263 the multiple CTM simulations that use state-of-the-science representations of O₃ and PM_{2.5} chemistry, 264 these indicators were assumed to represent the true condition for comparison with the condition predicted 265 266 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 267 prediction is indicated by the observable indicator providing consistent results for O3 or PM2.5 chemistry 268

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:

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

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:

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

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.

284 **3. Results**

3.1. Evaluating observable indicator performance in predicting chemistry regimes

286 **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 H₂O₂/HNO₃ approximately 73.4 %, with a value of 0.2 for the transition from NO_x-saturated to NO_x- 291 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 292 H₂O₂/HNO₃ could be increased to 80.5 % if 0.3 was used as the transition value. This finding was 293 consistent with corresponding findings in previous studies, which have suggested the transition values of 294 H_2O_2/HNO_3 within the range of 0.2-3.6 at different locations and in different seasons (Sillman, 1995; 295 296 Sillman et al, 1997; Lu and Chang, 1998; Tonnesen and Dennis, 2000; Hammer et al, 2002; Liang et al, 2006; Zhang et al., 2009). H₂O₂/(O₃+NO₂), with a transition value of 0.02, also exhibited a high annual 297 success rate of 66.4 %; this rate could be increased to 71.1 % by applying a transition value of 0.005 298 299 because the original transition value was too high, particularly in January, April, and October (see Fig. 4b). HCHO/NO_v and HCHO/NO₂ exhibited relatively low performance, particularly in April and July, because 300 the original transition values appeared to be too high (Fig. 4h and i). However, the performance of 301 HCHO/NO_v and HCHO/NO₂ could be greatly improved by using lower transition values, with increased 302 annual success rates as high as 76 %. The change of the transition values implies that such indicators 303 cannot fully consider all factors that determine the O_3 chemistry by using concentrations of just two 304 species. The transition values of the indicators NO_y, O₃/NO_x, O₃/NO_y, and O₃/NO_z were suitable for 305 estimating annual levels if only one unique transition value was applied for all months (apparently, these 306 307 transition values for O_3/NO_x , O_3/NO_v 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 308 inferior performance of the three O₃-involved indicators (O₃/NO_x, O₃/NO_y and O₃/NO_z) may have been 309 310 associated with the considerable effects of background O₃, which cannot be removed easily.

Because $H_2O_2/(O_3+NO_2)$ and HCHO/NO₂ exhibited good performance in predicting O₃ 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 314 suggested that HCHO is approximately proportional to the VOC reactivity (i.e., the weighted sum of the 315 reactions of VOCs with OH) and that HCHO/NO₂ closely approximates the competition between OH 316 reactions with VOC and NO₂ that is central to O_3 chemistry. H₂O₂ derives from a key radical termination 317 pathway under low NO_x conditions (HO₂ + HO₂ \rightarrow H₂O₂ + O₂). Comparison of H₂O₂ with NO_y or HNO₃, 318 which derives from a key radical termination pathway under high NO_x conditions, $OH + NO_2 \rightarrow HNO_3$) 319 represents the relative abundance of VOCs to NO_x. The new hybrid indicator incorporates information 320 from the two individual indicators and could potentially be more robust. 321

322 3.1.2 PM_{2.5}

We selected the GR and AdjGR as observable indicators for PM2.5 chemistry to identify NH3-poor 323 or NH₃-rich conditions. Comparison of GR and AdjGR with the FR is detailed in Fig. 5. AdjGR 324 performance was much higher than that of the GR, with a larger annual success rate of 74.1 % compared 325 with the GR's 55.6 % (see Table 3). The transition value of the GR appeared to be too low in all months 326 (Fig. 5a). This result was consistent with those of previous studies; the AdjGR tends to be a more robust 327 indicator because in contrast to the GR, it does not require an assumption of full sulfate neutralization 328 (Zhang et al., 2009). The improvement of AdjGR compared to GR is the greatest in January and the 329 smallest in July (Table 3). This is consistent with Pinder et al. (2008) who showed that accounting for 330 DSN is important under cold temperatures but GR and AdjGR converge for higher temperatures. 331

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

334
$$TAR = \frac{[TA]^2}{[TN] \times [TS]} = \frac{[NH_3] \times [NH_4^+]}{([HNO_3] + [NO_3^-]) \times [SO_4^{2^-}]},$$
(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 $[NH_4^+]$.

The performance of TAR in predicting $PM_{2.5}$ chemistry was slightly higher than that of AdjGR, as demonstrated by the higher success rate of TAR than that of AdjGR in all months. The annual success rate 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 O₃

Fig. 6 presents the log-linear regressions of the O3 observable indicators on the PR indicator derived 344 from the RSM. In general, all observable indicators exhibited strong correlations with the PR (all except 345 NO_v presented positive correlations with the PR), with varying R^2 values (0.08 - 0.75). The indicators 346 including NOy, O3/NOx, O3/NOy, and O3/NOz, which had relatively low success rates, exhibited weaker 347 correlation with the PR ($R^2 < 0.31$; Fig. 6c-f). The newly developed H₂O₂×HCHO/NO₂ indicator exhibited 348 the strongest correlation with the PR ($R^2 = 0.75$), implying that the log-linear combination of the H₂O₂, 349 HCHO, and NO₂ baseline concentrations could approximate the responsive PR indicator to quantify O₃ 350 chemistry. Other indicators can also be used to approximately estimate the PR based on the regression 351 coefficients shown in Fig. 6; however, their correlations with the PR were not as strong as those with 352 $H_2O_2 \times HCHO/NO_2$. 353

To evaluate the ability of the observable PR (oPR; estimated based on $H_2O_2 \times HCHO/NO_2$) to represent the spatial and temporal variation of O_3 chemistry, the spatial distribution of the PR and oPR in the four study months was compared across the simulated domain (Fig. 7). The oPR successfully captured 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 O₃ chemistry, even on a large spatial and temporal scale.

363 3.2.2. PM_{2.5}

The correlations between PM_{2.5} observable indicators and the responsive FR indicator derived from 364 the RSM were investigated (Fig. 8). The AdjGR has the lowest R^2 (0.40) because of its high variations for 365 366 the NH₃-poor condition (Fig. 5b). A stronger positive correlation was noted between the GR and FR (\mathbb{R}^2) = 0.57); however, the success rate of the GR was the lowest among all the indicators (the success rate of 367 the GR increased when the transition value was set as the median value of the GR, namely 5, at an FR of 368 369 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, 370 nitric acid gas, particulate ammonium, sulfate, and nitrate. 371

The capability of the observable FR (oFR; estimated based on the TAR indicator) in representing 372 the spatial and temporal variation of PM_{2.5} chemistry is illustrated in Fig. 9. Both the FR and oFR 373 suggested strong NH₃-poor condition (FR > 1) in January and NH₃-rich condition (FR < 1) in April and 374 July. The oFR suggested strong NH₃-rich condition in northern and eastern China and the Sichuan Basin; 375 these findings were consistent with those for the FR. The domain-averaged oFRs were 1.56, 1.05, 0.86, 376 377 and 1.24 in January, April, July, and October, respectively, with the strongest NH₃-poor condition in January and NH₃-rich condition in July. These findings were comparable with the FRs of 1.47, 1.16, 0.95, 378 and 1.19 for the four study months, respectively, suggesting that the oFR can approximate the FR to 379 380 quantify the PM_{2.5} chemistry and its spatial and temporal variations.

381 3.3. Policy implications

382 **3.3.1. O**₃

The responsive PR indicator may help policy-makers to understand the status and extent of O₃ 383 chemistry in the current scenarios. A lower PR (< 1) suggested a NO_x-saturated regime. Moreover, the 384 VNr could be used to inform policy-makers about the level of simultaneous control of VOCs required to 385 prevent an increase in O_3 levels from NO_x controls. In general, the VNr is negatively correlated with the 386 PR because a lower PR implies a stronger NO_x-saturated regime, which in turn requires more simultaneous 387 VOC control with NO_x. By contrast, a higher PR implies a weaker NO_x-saturated or even NO_x-limited 388 389 regime, which requires less or no simultaneous control of VOCs with NOx. The negative correlation between VNr and the PR was quantified by the simple linear regression of VNr on PR (Fig. S7). A high 390 R² (approximately 0.82) suggested that the VNr originally derived from the RSM can also be 391 392 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 domainaveraged 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).

407 **3.3.2.** PM_{2.5}

Using the responsive FR indicator or its observable oFR indicator can rapidly identify NH₃-rich or 408 409 NH₃-poor conditions, and this information can aid policy-makers in estimating the additional PM_{2.5} benefit associated with simultaneous control of NH₃ and NO_x emissions (Δ C NH₃). As discussed in Section 2.2, 410 ΔC NH₃ can be calculated from the RSM using the first derivative of the PM_{2.5} responsive function to 411 412 NH₃. Therefore, ΔC NH₃ must be strongly associated with the secondary inorganic aerosol (SNA) concentration, as suggested in Fig. S8, which demonstrates a strong correlation between SNA 413 concentration and ΔC NH₃. The linear regression with high R² (>0.71) implies that the ΔC NH₃ can be 414 approximately calculated based on the SNA concentration. 415

The ΔC NH₃ estimated based on the SNA concentration (o ΔC NH₃; based on the regression 416 function in Fig. S8) was compared with that derived from the RSM (Fig. 12). The $o\Delta C$ NH₃ typically 417 captured the spatial and temporal variation of ΔC NH₃, suggesting large benefits in January and October, 418 particularly in eastern China and the Sichuan Basin. The domain-averaged $\Delta C NH_3$ values were 419 approximately 0.31, 0.22, 0.16, and 0.38 µg m⁻³ PM_{2.5} per 10 % NH₃ reduction in January, April, July, and 420 October respectively. In April and July, $o\Delta C$ NH₃ presented consistent results approximately 0.21 and 421 0.16 µg m⁻³ PM_{2.5}, respectively, per 10 % NH₃ reduction, but slightly underestimated the benefits in 422 January and October (0.24 and 0.22 µg m⁻³ PM_{2.5}, respectively, per 10 % NH₃ reduction). 423

424 At the annual level, ΔC_NH_3 was compared with the population-weighted PM_{2.5} concentration in 425 each province (Fig. 13). ΔC_NH_3 ranged from 2 to 12 µg m⁻³ PM_{2.5} per 10 % NH₃ reduction. In addition, 426 the provinces with higher PM_{2.5} exposure exhibited additional benefits from NH₃ 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 % NH₃ reduction. These benefits from simultaneous NH₃ 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 O₃ and PM_{2.5}

432 NO_x and VOCs are major precursors for O₃ and PM_{2.5}, and effectively controlling their emissions can lead to cobenefits in reducing O₃ and PM_{2.5}. The PR results suggest strong NO_x-saturated regimes in 433 northern and eastern China including key regions such as the Sichuan Basin, YRD, and PRD, where 434 435 simultaneous VOC control with a certain VOC-to-NO_x ratio is required to prevent increases in O₃ levels from the NO_x controls. PM_{2.5} sensitivity to NO_x can be negative under a strong NO_x-saturated regime; this 436 effect is not as significant as it is for O₃ (Fig. 3). We quantified the nonlinearity of PM_{2.5} sensitivity to NO_x 437 438 by using the same PR concept but for PM_{2.5} response (Text S2); Fig. S9 presents the spatial distribution 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} 439 were > 1 in April, July, and October in all grid cells across China, suggesting that NO_x control is always 440 beneficial for PM_{2.5} reduction during these months. Even in January, the PR for PM_{2.5} (0.4-0.8 in eastern 441 and northern China) remains larger than that for O_3 (0.2-0.6 in eastern and northern China), implying that 442 the suggested VNr for O₃ was high enough to overcome the potential limitations on PM_{2.5} reduction from 443 NO_x control. 444

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). 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 $PM_{2.5}$ 450 and O3 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 451 this case might be associated with the smaller PR for PM_{2.5} as well as the additional benefit of VOC 452 controls in reducing secondary organic aerosols. Apparently, a larger VNr control ratio and greater 453 emission control is required in January compared with other months. In Fig. 14(a), only one pathway can 454 455 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 456 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 457 458 was dominant, the NO_x control was critical because the VOC controls had little effect on either O₃ or PM_{2.5}. At the annual level, the simultaneous VOC controls (40 % of the NO_x controls) led to cobenefits in 459 reducing both O3 and PM2.5 at the national level. However, VNr varied significantly in different seasons, 460 suggesting that considering the seasonality of O_3 and $PM_{2.5}$ chemistry is necessary for design of a season-461 specific control strategy. 462

463

4. Summary and conclusion

464 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 465 useful as the RSM-based PR and FR indicators for policy-makers to infer feasible emission reduction 466 467 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 468 quantify the nonlinearity of O3 and PM2.5 response to precursor emissions. Similar to the traditional 469 470 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 471 satellite retrievals. In addition, the observable responsive indicators can not only rapidly identify the 472

chemical regime but also provide policy-makers with useful information, such as simultaneous VOC controls to prevent increases in O₃ levels from NO_x controls under the NO_x-saturated regime (i.e., VNr), as well as the additional benefit of simultaneously reducing NH₃ 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 O₃-chemistry indicator, namely $H_2O_2 \times HCHO/NO_2$, and PM_{2.5}-chemistry 480 481 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 NO₂ 482 concentrations could provide an approximate PR to quantify O₃ chemistry spatially and temporally. 483 Similarly, the log-linear combination of baseline concentrations of ammonia gas, nitric acid gas, 484 particulate ammonium, sulfate and nitrate can be used to approximately estimate the FR for PM2.5 485 chemistry. The VNr was highly correlated with the PR, suggesting that a stronger NO_x -saturated regime 486 requires greater VOC control accompanied by NO_x control. The positive correlation between ΔC NH₃ 487 and the population-weighted PM_{2.5} concentration suggested that a province with high PM_{2.5} exposure can 488 489 gain greater benefits from NH₃ 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 490 cobenefits of reducing both O₃ and PM_{2.5}. However, VNr varied significantly among the seasons and 491 492 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 493 and the responsive indicator might also be influcenced by uncertainties in the chemical mechanism of 494 495 CMAQ as well as prediction errors of the pf-RSM. The new indicators were designed based on the existing

496 chemical mechanism, and the transition values might be refined in the future as our understanding of497 atmospheric chemical processes improves.

In conclusion, the two unique aspects of this study are as follows. First, quantification of the 498 correlation of observable indicators with responsive indicators (Fig. 5 and 7) implied that the traditional 499 observable indicators, based on monitored or satellite-retrieved concentrations, can be used to quantify 500 the nonlinearity of PM_{2.5} and O₃ to precursor emission and provide useful policy implications. Second, 501 this study reported a promising method for efficiently establishing PM_{2.5}- and O₃- responsive functions to 502 precursors for traditional responsive or reduced-form modeling studies. This study suggested that the PR 503 504 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 505 polynomial functions can be calculated based on a set of ambient concentrations of certain chemical 506 species. The simple log-linear regression method used in this study demonstrated the possibility that even 507 in the presence of uncertainties in prediction, more advanced data analytics technologies such as deep 508 learning may improve performance in future. 509

510

511 **Data availability**

512

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

513 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.

518 Acknowledgements

519 This work was supported in part by National Key R & D program of China (2017YFC0210006),

520 National Natural Science Foundation of China (21625701&51861135102), National Research Program

521 for Key Issues in Air Pollution Control (DQGG0301& DQGG0204), and Shanghai Environmental

522 Protection Bureau (2016-12). This work was completed on the "Explorer 100" cluster system of Tsinghua

523 National Laboratory for Information Science and Technology.

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525 Disclaimer

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Term	O ₃	PM _{2.5}
1	NO _x ⁵	VOC
2	NO_x^4	NH ₃
3	NO_x^3	$\rm NH_3^2$
4	NO_x^2	$\rm NH_3{}^3$
5	NO _x	SO_2
6	VOC	$\rm VOC^2$
7	VOC^2	NO _x VOC
8	VOC^3	NO _x ² VOC
9	NO _x VOC	NO _x ⁴ VOC
10	NO _x VOC ³	NO _x NH ₃
11	NO _x ⁵ VOC	NO _x
12	NO _x ² VOC	NO_x^2
13	SO_2	NO_x^3
14	NH ₃	NO _x ⁴

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

Indicator		success rate at TV (%)				success rate at TV' (%)				⁄0)		
	TV*	Jan	Apr	Jul	Oct	ANN	TV'	Jan	Apr	Jul	Oct	ANN
H ₂ O 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
NOy	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 ₂ O ₂ ×HCHO/NO ₂	-	-	-	-	-	-	0.3	92.3	81.6	89.5	86.0	87.3

Table 2. Summary of observable indicators and their performances in predicting O₃ chemistry

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

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	

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

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

** TV- transition value as proposed in this study



Figure 1. Flow of observable response indicator development and application



Figure 2. Simulation domain over mainland China (27 × 27-km² 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 $\mu g m^{-3}$ for $PM_{2.5}$ and ppb for O_3)





711Figure 4. Performance of observable indicators in predicting O_3 chemistry. The x-axis represents the PR712values where the transition value is 1, and the y-axis represents the observable indicators. The blue dots713represent the grids where O_3 chemistry is successfully predicted by the observable indicator; the red dots714represent the grids where the observable indicator fails to predict O_3 chemistry. The numbers in the four715corners represent the grid number in each section; the number in July is much lower than those in the716other months because most grids are located at the NOx-limited regime with PR > 2 in July.



Figure 5. Performance of observable indicators in predicting PM_{2.5} chemistry. The x-axis represents the
 FR values where the transition value is 1, and the y-axis represents the observable indicators. The blue
 dots represent the grids where PM_{2.5} chemistry is successfully predicted by the observable indicator; the
 red dots represent the grids where the observable indicator fails to predict PM_{2.5} chemistry. The numbers
 in the four corners represent the grid number in each section; the number in January is much lower than
 those in the other months because most grids are located at the NH₃-poor condition with FR>2 in



Figure 6. Development of observable responsive indicators for O₃ chemistry based on log-linear
 regressions between observable indicators and the PR.



Figure 7. Comparison of the PR derived from the RSM with that calculated from concentrations for O₃
 chemistry. The oPR was estimated based on H₂O₂×HCHO/NO₂.



Figure 8. Development of observable responsive indicators for PM_{2.5} chemistry based on log-linear
 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



741Figure 12. Comparison of the benefit in reducing $PM_{2.5}$ from simultaneous NH_3 reduction (ΔC_NH_3)742with that calculated from concentrations ($o\Delta C_NH_3$)



Figure 13. Comparison of annual-averaged benefit in reducing PM_{2.5} from simultaneous NH₃ reduction
 (ΔC_NH₃) 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 O₃ concentrations (in µg m⁻³) in China (NO_x is from no control to 80 % reduction)