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

Jia Xing1,2, Dian Ding1,2, Shuxiao Wang1,2, Zhaoxin Dong1,2, James T. Kelly3, Carey Jang3, Yun Zhu4, and Jiming Hao1,2

1State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China
2State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, China
3Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, USA
4College of Environmental Science & Engineering, South China University of Technology, Guangzhou Higher Education Mega Center, Guangzhou, China

Correspondence: Shuxiao Wang (shxwang@tsinghua.edu.cn)

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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$_2$O$_2$ × 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 conditions in January and NH$_3$-rich conditions in April and July, as well as NH$_3$-rich conditions 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 1.2 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.

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, 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 al., 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$_2$O$_2$/HNO$_3$, HCHO/NO$_2$ and H$_2$O$_2$/([O$_3$]+NO$_2$) (Milford et al., 1994; Sillman, 1995; Tonnesen and Dennis, 2000; Sillman and He, 2002), which can be used to identify NO$_y$-saturated or NO$_x$-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 and Baldasano, 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 the Supplement Sect. S1) to identify NH$_3$-poor or NH$_3$-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 a 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, 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., 2019). The rate of increase in O$_3$ concentration (based on the 90th percentile of a daily maximum of 8 h 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\textsubscript{3} and PM\textsubscript{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: Sect. 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\textsubscript{3} and PM\textsubscript{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 were analyzed based on the monthly average for afternoon O\textsubscript{3} (12:00–18:00 China standard time when O\textsubscript{3} was the highest across a day) and monthly average for 24 h PM\textsubscript{2.5}. To approximate exposure concentrations, we also estimated population-weighted O\textsubscript{3} and PM\textsubscript{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 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 planetary boundary layer (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\textsubscript{3} and PM\textsubscript{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).
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 $\pm 60\%$). 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 multiregional 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, 2018; Wang et al., 2011; 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 the 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:

$$
\Delta \text{Conc} = \sum_{i=1}^{n} X_i \cdot (\Delta E_{NO_x})^{a_i} \cdot (\Delta E_{SO_2})^{b_i} \cdot (\Delta E_{NH_3})^{c_i} \cdot (\Delta E_{\text{VOCs}})^{d_i},
$$

where $\Delta \text{Conc}$ is the change in O$_3$ or PM$_{2.5}$ concentration from the baseline concentration calculated from a polynomial function of four variables ($\Delta E_{NO_x}$, $\Delta E_{SO_2}$, $\Delta E_{NH_3}$, $\Delta E_{\text{VOCs}}$); $\Delta E_{NO_x}$, $\Delta E_{SO_2}$, $\Delta E_{NH_3}$, and $\Delta E_{\text{VOCs}}$ are the change ratios of NO$_x$, SO$_2$, NH$_3$, and VOC emissions (i.e., $\Delta \text{Emissions/Baseline \_Emissions}$), respectively, relative to the baseline emissions (baseline = 0); and $a_i$, $b_i$, $c_i$, and $d_i$ are the nonnegative integer powers of $\Delta E_{NO_x}$, $\Delta E_{SO_2}$, $\Delta E_{NH_3}$, and $\Delta E_{\text{VOCs}}$, 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 Tables S3 and S4, respectively. The terms with the first degree for NO$_x$, 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 $X_3$) and VOCs (term $X_6$) than to SO$_2$ (term $X_{12}$) 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$_3$ and 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.

$\Delta C_{NH_3}$ (the unit is micrograms per cubic meter of PM$_{2.5}$ per 10 % NH$_3$ reduction) can be calculated as follows:

$$\Delta C_{NH_3} = X_2 \times 0.1.$$  

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).

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 micrograms per cubic meter for PM$_{2.5}$ and parts per billion for O$_3$.)
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.
For O₃, the PR can be directly calculated as follows:

\[
PR = 1 + \Delta E_{NO_x} \big|_{\frac{\partial \Delta \text{ConcO}_3}{\partial \text{NO}_x}=0} = E_{NO_x} \epsilon [a, b],
\]

(3)

where \( \frac{\partial \Delta \text{ConcO}_3}{\partial \text{NO}_x} \) is the first derivative of the \( \Delta \text{ConcO}_3 \) to \( \Delta E_{NO_x} \), which can be derived as follows:

\[
5 \cdot X_1 \cdot \Delta E_{NO_x}^4 + 4 \cdot X_2 \cdot \Delta E_{NO_x}^3 + 3 \cdot X_3 \cdot \Delta E_{NO_x}^2 \\
+ 2 \cdot X_4 \cdot \Delta E_{NO_x} + X_5 = 0
\]

(4)

The PR is the NOₓ emissions (represented as \( 1 + \Delta E_{NO_x} \)) that produce maximum O₃ concentration under the baseline VOC emissions. For PR < 1, the baseline condition is NOₓ saturated, and the level of simultaneous control of VOCs to prevent an increase in O₃ levels from the NOₓ controls must be understood. This level is defined by the ratio of VOCs to NOₓ (i.e., VNr) corresponding to the PR and is calculated as follows:

\[
\text{VNr} = r \big|_{\frac{\partial \Delta \text{ConcO}_3}{\partial \text{NO}_x}=0} \text{ when } PR < 1, r = \Delta E_{VOC}/\Delta E_{NO_x},
\]

(5)

where \( \frac{\partial \Delta \text{ConcO}_3}{\partial \text{NO}_x} \) is the first derivative of the \( \Delta \text{ConcO}_3 \) to \( \Delta E_{NO_x} \). When \( \Delta E_{VOC} = r \times \Delta E_{NO_x} \), and \( \Delta E_{SO_2} \) and \( \Delta E_{NH_3} \) are 0, \( \frac{\partial \Delta \text{ConcO}_3}{\partial \Delta E_{NO_x}} \) can be written as follows:

\[
5 \cdot X_1 \cdot \Delta E_{NO_x}^4 + 4 \cdot X_2 \cdot \Delta E_{NO_x}^3 + 3 \cdot X_3 \cdot \Delta E_{NO_x}^2 + 2 \cdot X_4 \cdot \Delta E_{NO_x} + X_5 = 0
\]

(6)

Since the \( \Delta E_{NO_x} \) is close to 0 when the controls are taken from the baseline, we ignore the terms of \( \Delta E_{NO_x} \) in the first derivative function above, and then it can be written as follows,

\[
X_5 + X_6 \cdot r = 0.
\]

(7)

The VNr therefore can be calculated using the following equation:

\[
\text{VNr} = \frac{X_5}{X_6}.
\]

(8)

For PM₂·₅, the FR can be directly calculated from the polynomial function of PM₂·₅ by estimating the second derivative of the PM₂·₅ 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
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 in the NH$_3$-poor conditions with FR $> 2$ in January.

Figure 6. Development of observable responsive indicators for O$_3$ chemistry based on log-linear regressions between observable indicators and the FR.
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):

\[
FR = 1 + \Delta E_{NH_3} \left( \frac{\partial \Delta Conc_{PM}}{\partial E_{NH_3}} \cdot \frac{\Delta E_{NH_3}}{\Delta E_{NO_x}} \right) \epsilon [a, b],
\]

\[
\Delta E_{NO_x} = 0,
\]

where \(\frac{\partial \Delta Conc_{PM}}{\partial E_{NH_3}}\) and \(\frac{\partial \Delta Conc_{PM}}{\partial E_{NO_x}}\) are the first derivatives of the \(\Delta Conc_{PM}\) to \(\Delta E_{NH_3}\) and \(\Delta E_{NO_x}\), respectively, and \(\Delta E_{NH_3}\) can be obtained as follows:

\[
3 \cdot X_4 \cdot \Delta E_{NH_3}^2 + (2 \cdot X_3 - X_{10}) \cdot \Delta E_{NH_3} + X_2 - X_{11} = 0.
\]

The FR is the NH$_3$ emissions (represented as \(1 + \Delta E_{NH_3}\)) that correspond to the inflection point between NH$_3$-rich and NH$_3$-poor conditions under baseline NO$_x$ 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 \(\Delta C_{\_NH_3}\)) from simultaneous NH$_3$ controls in the
same percentage as the required NOx controls can be quantified as follows:

$$\Delta C_{\text{NH}_3} = \left( \frac{\partial \Delta \text{Conc} _{\text{PM}_{2.5}}}{\partial \Delta \text{E}_{\text{NO}_x}} \bigg|_{\Delta \text{E}_{\text{NH}_3}=\Delta \text{E}_{\text{NO}_x}} \right) - \left( \frac{\partial \Delta \text{Conc} _{\text{PM}_{2.5}}}{\partial \Delta \text{E}_{\text{NO}_x}} \bigg|_{\Delta \text{E}_{\text{NH}_3}=0} \right),$$

where $\frac{\partial \Delta \text{Conc} _{\text{PM}_{2.5}}}{\partial \Delta \text{E}_{\text{NO}_x}} \bigg|_{\Delta \text{E}_{\text{NH}_3}=\Delta \text{E}_{\text{NO}_x}}$ is the first derivative of the $\Delta \text{Conc} _{\text{PM}_{2.5}}$ response to $\Delta \text{E}_{\text{NO}_x}$ when $\Delta \text{E}_{\text{NH}_3} = \Delta \text{E}_{\text{NO}_x}$, and $\frac{\partial \Delta \text{Conc} _{\text{PM}_{2.5}}}{\partial \Delta \text{E}_{\text{NO}_x}} \bigg|_{\Delta \text{E}_{\text{NH}_3}=0}$ is the first derivative of the $\Delta \text{Conc} _{\text{PM}_{2.5}}$ response to $\Delta \text{E}_{\text{NO}_x}$ when $\Delta \text{E}_{\text{NH}_3} = 0$.

### 2.3 Observable indicators of $\text{O}_3$ and PM$_{2.5}$ chemistry

Zhang et al. (2009) summarized the various observable indicators with their corresponding transition values to identify $\text{O}_3$ and PM$_{2.5}$ chemistry: $\text{O}_3$ indicators were $\text{H}_2\text{O}_2/\text{HNO}_3$, $\text{H}_2\text{O}_2/(\text{O}_3 + \text{NO}_2)$, $\text{NO}_y$, $\text{O}_3/\text{NO}_x$, $\text{O}_3/\text{NO}_y$, $\text{O}_3/\text{NO}_x$, $\text{HCHO}/\text{NO}_y$, and $\text{HCHO}/\text{NO}_x$, 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 original 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 $\text{O}_3$ 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 $\text{O}_3$ 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 $\text{O}_3$ or PM$_{2.5}$ chemistry as suggested 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:

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

where $Y$ is an observable indicator for $\text{O}_3$ or PM$_{2.5}$, $X$ is the RSM-based indicator (i.e., PR for $\text{O}_3$ 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:

$$X' = \log (Y) - B \cdot A^{-1}.$$

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 traditional RSM-based indicators.

Figure 8. Development of observable responsive indicators for PM$_{2.5}$ chemistry based on log-linear regressions between observable indicators and the FR.
3 Results

3.1 Evaluating observable indicator performance in predicting chemistry regimes

3.1.1 O₃

Observable indicators and the PR are compared in Fig. 4, and the performance of observable indicators in predicting O₃ 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 at approximately 73.4 %, with a value of 0.2 for the transition from NOₓ-saturated to NOₓ-limited conditions. However, the original transition value of 0.2 for H₂O₂/HNO₃ tended to be too low, particularly in April, July and October (see Fig. 4a). This study found that the annual success rate of H₂O₂/HNO₃ 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 H₂O₂/HNO₃ to be within the range of 0.2–3.6 at different locations and in different seasons (Sillman, 1995; Sillman et al., 1997; Lu and...
Figure 10. Comparison of VNr with oVNr.

Chang, 1998; Tonnesen and Dennis, 2000; Hammer et al., 2002; Liang et al., 2006; Zhang et al., 2009). \( \text{H}_2\text{O}_2/\left(\text{O}_3 + \text{NO}_2\right) \), 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). \( \text{HCHO}/\text{NO}_y \) and \( \text{HCHO}/\text{NO}_2 \) exhibited relatively low performance, particularly in April and July, because the original transition values appeared to be too high (Fig. 4g and h). However, the performance of \( \text{HCHO}/\text{NO}_x \) and \( \text{HCHO}/\text{NO}_2 \) 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 \( \text{O}_3 \) chemistry by using concentrations of just two species. The transition values of the indicators \( \text{NO}_y, \text{O}_3/\text{NO}_x, \text{O}_3/\text{NO}_y \) and \( \text{O}_3/\text{NO}_z \) were suitable for estimating annual levels if only one unique transition value was applied for all months (apparently, these transition values for \( \text{O}_3/\text{NO}_x, \text{O}_3/\text{NO}_y \) and \( \text{O}_3/\text{NO}_z \) in January and \( \text{NO}_x \) 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 \( \text{O}_3 \)-involved indicators (\( \text{O}_3/\text{NO}_x, \text{O}_3/\text{NO}_y \) and \( \text{O}_3/\text{NO}_z \)) may
have been associated with the considerable effects of background \( \text{O}_3 \), which cannot be removed easily.

Because \( \text{H}_2\text{O}_2/(\text{O}_3 + \text{NO}_2) \) and HCHO/\( \text{NO}_2 \) exhibited good performance in predicting \( \text{O}_3 \) chemistry, this study proposed a new indicator combining these two indicators, namely \( \text{H}_2\text{O}_2 \times \text{HCHO}/\text{NO}_2 \), 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 (Stillman, 1995; Tonnensen 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/\( \text{NO}_2 \) closely approximates the competition between OH reactions with VOC and \( \text{NO}_2 \) that is central to \( \text{O}_3 \) chemistry. \( \text{H}_2\text{O}_2 \) derives from a key radical termination pathway under low-\( \text{NO}_x \) conditions (\( \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_3 \)). Comparison of \( \text{H}_2\text{O}_2 \) with \( \text{NO}_2 \) or \( \text{HNO}_3 \), which derives from a key radical termination pathway under high-\( \text{NO}_x \) conditions (\( \text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3 \)), represents the relative abundance of VOCs to \( \text{NO}_2 \). The new hybrid indicator incorporates information from the two individual indicators and could potentially be more robust.

### 3.1.2 \( \text{PM}_{2.5} \)

We selected the GR and AdjGR as observable indicators for \( \text{PM}_{2.5} \) chemistry to identify \( \text{NH}_3 \)-poor or \( \text{NH}_3 \)-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:

\[
\text{TAR} = \frac{[\text{TA}]^2}{[\text{TN}] \times [\text{TS}]} = \frac{[\text{NH}_3] \times [\text{NH}_3^+]^2}{([\text{HNO}_3] + [\text{NO}_2^+]) \times [\text{SO}_4^{2-}]},
\]

where [TN] and [TS] are the total molar concentrations of nitrate ([\( \text{HNO}_3 \] + [\( \text{NO}_2^+ \)]) and sulfate ([\( \text{SO}_4^{2-} \)]) , respectively, and TAR is the relative abundance of total ammonia to nitrate and sulfate, regarded as the product of [TA]/[TN] and [TA]/[TS]. To simplify the calculation, \([\text{TA}]^2 \) is assumed to be the product of the molar concentration of ammonia gas [\( \text{NH}_3 \)] and ammonium [\( \text{NH}_3^+ \)].

The performance of TAR in predicting \( \text{PM}_{2.5} \) 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).

### 3.2 Developing the observable responsive indicators

#### 3.2.1 \( \text{O}_3 \)

Figure 6 presents the log-linear regressions of the \( \text{O}_3 \) observable indicators on the PR indicator derived from the RSM. In general, all observable indicators exhibited strong correlations with the PR (all except \( \text{NO}_x \) presented positive correlations with the PR), with varying \( R^2 \) values (0.08–0.75). The indicators including \( \text{NO}_x \), \( \text{O}_3/\text{NO}_x \), \( \text{O}_3/\text{NO}_x \), and \( \text{O}_3/\text{NO}_x \), which had relatively low success rates, exhibited weaker correlation with the PR (\( R^2 < 0.31 \); Fig. 6c–f). The newly developed \( \text{H}_2\text{O}_2 \times \text{HCHO}/\text{NO}_2 \) indicator exhibited the strongest correlation with the PR (\( R^2 = 0.75 \)), implying that the log-linear combination of the \( \text{H}_2\text{O}_2 \), HCHO and \( \text{NO}_2 \) baseline concentrations could approximate the responsive PR indicator to quantify \( \text{O}_3 \) chemistry. Other indicators can also be used to approximately estimate the PR based on the regression coefficients shown in Fig. 6; however, their correlations with the PR were not as strong as those with \( \text{H}_2\text{O}_2 \times \text{HCHO}/\text{NO}_2 \).

To evaluate the ability of the observable PR (oPR; estimated based on \( \text{H}_2\text{O}_2 \times \text{HCHO}/\text{NO}_2 \)) to represent the spatial and temporal variation in \( \text{O}_3 \) 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 \( \text{NO}_3^- \)-saturated regime in January (PR < 1) and the \( \text{NO}_3^- \)-limited (PR > 1) regime in July.

In addition, the PR and oPR suggested a consistently strong \( \text{NO}_3^- \)-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\textsubscript{3} chemistry, even on a large spatial and temporal scale.

### 3.2.2 PM\textsubscript{2.5}

The correlations between PM\textsubscript{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\textsubscript{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 concentra-

![Figure 12](https://example.com/figure12.png)

**Figure 12.** Comparison of the benefit in reducing PM\textsubscript{2.5} from simultaneous NH\textsubscript{3} reduction ($\Delta C_{\text{NH}_3}$) with that calculated from concentrations ($o\Delta C_{\text{NH}_3}$).
tions 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 in PM$_{2.5}$ chemistry is illustrated in Fig. 9. Both the FR and oFR suggested strong NH$_3$-poor conditions (FR > 1) in January and NH$_3$-rich conditions (FR < 1) in April and July. The oFR suggested strong NH$_3$-rich conditions 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 conditions in January and NH$_3$-rich conditions 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 policymakers 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$_2$O$_2$ × 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. This is comparable with VNr in the four study months (i.e., 0.82, 0.46, 0.34, and 0.57, respectively).

The annually 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 provinces 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 ($\Delta C_{\text{NH}_3}$). As discussed in Sect. 2.2, $\Delta C_{\text{NH}_3}$ can be calculated from the RSM using the first derivative of the PM$_{2.5}$ responsive function to NH$_3$. Therefore, $\Delta C_{\text{NH}_3}$ 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 $\Delta C_{\text{NH}_3}$. The linear regression with high $R^2$ (> 0.71) implies that the $\Delta C_{\text{NH}_3}$ can be approximately calculated based on the SNA concentration.

The $\Delta C_{\text{NH}_3}$ estimated based on the SNA concentration ($\alpha\Delta C_{\text{NH}_3}$; based on the regression function in Fig. S8) was compared with that derived from the RSM (Fig. 12). The $\alpha\Delta C_{\text{NH}_3}$ typically captured the spatial and temporal variation in $\Delta C_{\text{NH}_3}$, suggesting large benefits in January and October, particularly in eastern China and the Sichuan Basin.
The domain-averaged $\Delta C_{NH_3}$ values were approximately 0.31, 0.22, 0.16, and 0.38 $\mu$g m$^{-3}$ PM$_{2.5}$ per 10% NH$_3$ reduction in January, April, July, and October, respectively. In April and July, $\Delta C_{NH_3}$ presented consistent results of approximately 0.21 and 0.16 $\mu$g 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 $\mu$g m$^{-3}$ PM$_{2.5}$, respectively, per 10% NH$_3$ reduction).

At the annual level, $\Delta C_{NH_3}$ was compared with the population-weighted PM$_{2.5}$ concentration in each province (Fig. 13). $\Delta C_{NH_3}$ ranged from 0.2 to 1.2 $\mu$g 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 $\Delta C_{NH_3}$), particularly in Hunan, Shandong, Tianjin, Jiangxi, Anhui, Henan and Hubei where $\Delta C_{NH_3}$ was > 0.8 $\mu$g m$^{-3}$ PM$_{2.5}$ per 10% NH$_3$ reduction. These benefits from simultaneous NH$_3$ control were substantial enough to be considered in these regions for achieving the national ambient PM$_{2.5}$ target (35 $\mu$g m$^{-3}$).

3.3.3 Co-benefits of NO$_x$ and VOC control in reducing O$_3$ and PM$_{2.5}$

NO$_x$ and VOCs are major precursors for O$_3$ and PM$_{2.5}$, and effectively controlling their emissions can lead to co-benefits in reducing O$_3$ and PM$_{2.5}$. 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. PM$_{2.5}$ sensitivity to NO$_x$ can be negative under a strong NO$_x$-saturated regime; this effect is not as significant as it is for O$_3$ (Fig. 3). We quantified the non-linearity of PM$_{2.5}$ sensitivity to NO$_x$ by using the same PR concept but for PM$_{2.5}$ response (Sect. 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$_{2.5}$ were > 1 in April, July and October in all grid cells across China, suggesting that NO$_x$ control is always beneficial for PM$_{2.5}$ reduction during these months. Even in January, the PR for PM$_{2.5}$ (0.4–0.8 in eastern and northern China) remains larger than that for O$_3$ (0.2–0.6 in eastern and northern China), implying that the suggested VNr for O$_3$ was
high enough to overcome the potential limitations on PM$_{2.5}$ reduction from NO$_x$ control.

To explore the co-benefits 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$_{2.5}$ and O$_3$ require VOC emission controls in addition to NO$_x$ controls to prevent potential disbenefits associated with the non-linear 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. 14a, 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 the 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 co-benefits 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 traditionally observable indicators and developed new observable response indicators, the oPR and oFR, which can be used to quantify the non-linearity 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., $\Delta C_{\text{NH}_3}$). 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$_2$O$_2$ × 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$_2$O$_2$, 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 ammonia, 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 $\Delta C_{\text{NH}_3}$ 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 co-benefits 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 discrepancy between the observable indicator and the responsive indicator might also be influenced 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 (Figs. 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 from the corresponding author upon request.

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