

# Observable indicators of the sensitivity of PM<sub>2.5</sub> nitrate to emission reductions—Part I: Derivation of the adjusted gas ratio and applicability at regulatory-relevant time scales

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## Abstract

Chemical transport models have frequently been used to evaluate the impacts of emission reductions on inorganic PM<sub>2.5</sub>. However, such models are limited in their accuracy by uncertain estimates of the spatial and temporal characterization of emissions and meteorology. Site-specific observations can more accurately characterize the distribution of pollutants, but cannot predict the effectiveness of emission controls. In this research, we use equilibrium theory and a chemical transport model to find observable indicators that are robust predictors of the change in PM<sub>2.5</sub> nitrate due to changes in NH<sub>3</sub>, SO<sub>2</sub>, and NO<sub>x</sub> emissions. Two conditions are necessary: (1) the indicator must be valid at both instantaneous equilibrium and regulatory (daily and monthly) time-scales and (2) the indicator must be able to explain the majority of the spatial and temporal variance in the PM<sub>2.5</sub> nitrate sensitivity. We find that the ratio of free ammonia to total nitrate meets these conditions during the winter in the Eastern United States. This observable ratio can be used to predict the percent change in PM<sub>2.5</sub> nitrate due to SO<sub>2</sub> and NH<sub>3</sub> emissions reductions with nearly zero bias when compared with an emission driven chemical transport model. This permits a novel method for estimating the effectiveness of emission control strategies. The chemical transport model can be used to derive the relationship between the observed concentrations and the change in nitrate due to emission changes. Then observations can be used to apply that relationship to specific locations of interest. Published by Elsevier Ltd.

*Keywords:* Inorganic aerosol system; Particulate matter; Air-quality modeling; Impacts of emission reductions

## 1. Introduction

A significant fraction of fine particulate matter (PM<sub>2.5</sub>) in the Eastern United States is composed of

nitrate, especially in winter (McMurry et al., 2004). Because of the complex relationship between ammonium, sulfate, and nitrate (West et al., 1999; Vayenas et al., 2005), control of nitrate PM<sub>2.5</sub> continues to be a difficult challenge. Air-quality managers frequently employ chemical transport models (CTMs), which explicitly represent the emissions, chemical transformations, transport, and deposition of the species relevant to the formation and persistence of PM<sub>2.5</sub> nitrate. However, the

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predictions of these models depend on hourly estimates of emissions across the domain. For many species, these emission estimates are highly uncertain (NARSTO, 2005). Since many pollution sources are difficult to identify and quantify, such uncertainties are likely to persist for the foreseeable future.

We propose to use the CTM in a different manner. Rather than make precise predictions of the change in concentration due to an emission change, we use the CTM as a tool to understand the key features of the inorganic aerosol system. We are interested in identifying an observable indicator that quantitatively relates the sensitivity of PM<sub>2.5</sub> nitrate to a change in emissions. Such an indicator would allow us to estimate the sensitivity of the system using observations rather than models based on uncertain emission inventories. However, because these indicators are a simplification of the complex inorganic aerosol system, it is essential to conduct a full evaluation to ensure that they are robust across a range of atmospheric and chemical conditions and are predictive for the daily and monthly time-scales relevant to regulatory decision-making.

Ansari and Pandis (1998) and Blanchard et al. (2000) have developed indicators that use observable quantities to estimate the change in particle nitrate at *instantaneous equilibrium* given a change in *precursor concentrations* (NH<sub>3</sub>, HNO<sub>3</sub>, and SO<sub>4</sub><sup>2-</sup>). In this work, we seek to find similar indicators that estimate the change in *time-averaged* particle nitrate given a change in *emissions* (NH<sub>3</sub>, NO<sub>x</sub>, and SO<sub>2</sub>). The indicators we propose are of greater regulatory value, since the available policy mechanisms include emission reductions and the desired outcome is a reduction in time-averaged PM<sub>2.5</sub> nitrate.

In the first part of this series, we identify two indicators, examine the conditions under which they have predictive value, and evaluate their accuracy for predicting the change in particle nitrate concentration. In the second part of this series, we apply these indicators to predict the non-linear effect of sulfur dioxide emission reductions on particle nitrate given uncertainties in the atmospheric budgets of total nitrate and total ammonia.

### 1.1. Inorganic aerosol system

Nitrate is formed when NO and NO<sub>2</sub> (NO<sub>x</sub> ≡ NO + NO<sub>2</sub>) are oxidized to form nitric acid (HNO<sub>3</sub>). In the presence of ammonia, a fraction of the nitric

acid will partition to the particle phase to form ammonium nitrate aerosol.

Sulfate is formed by gas-phase and aqueous-phase oxidation of sulfur dioxide. Sulfate has a low vapor pressure and will condense to form sulfuric acid aerosol. Sulfuric acid aerosol is rarely found in ambient environments since ammonia will partially or fully neutralize the sulfate by forming either ammonium bisulfate or ammonium sulfate.

The extent to which ammonium nitrate is formed and sulfate is neutralized is governed by thermodynamic equilibrium. The equilibrium is determined by the temperature, relative humidity, and molar concentrations of total sulfate (TS ≡ SO<sub>4</sub><sup>2-</sup>), total nitrate (TN ≡ HNO<sub>3</sub> + NO<sub>3</sub><sup>-</sup>), and total ammonia (TA ≡ NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>). Under warm conditions, ammonium nitrate formation is not favorable, and the ammonium is largely associated with the available sulfate. Under cooler temperatures, ammonium nitrate is favorable and, given sufficient ammonia, a large fraction of the TN can be found in the particle phase.

Because the sulfate is often not fully neutralized, it is useful to define the degree of sulfate neutralization (DSN):

$$\text{DSN} = \frac{[\text{NH}_4^+](\text{mol}) - [\text{NO}_3^-](\text{mol})}{[\text{SO}_4^{2-}](\text{mol})}. \quad (1)$$

When there is sufficient ammonium to fully neutralize the sulfate, DSN = 2. Unlike the degree of neutralization (DON) which approximates the extent to which sulfate *and* nitrate are neutralized by ammonium (Adams et al., 1999), the DSN is an estimate of the neutralization of sulfate alone by ammonium. Note that in the absence of nitrate, both indices reduce to the ammonium-to-sulfate molar ratio.

In summary, the formation of inorganic PM is a two-step process. First, the primary emissions of NO<sub>x</sub> and SO<sub>2</sub> are oxidized to form aerosol precursors TN and TS, respectively. Second, a fraction of the TS, TN, and TA partition between the gas and particle phase according to thermodynamic equilibrium. Previous work (Ansari and Pandis, 1998; Blanchard et al., 2000) has focused on the thermodynamic equilibrium in the second step of this process. In this work, we seek to find indicators that are representative of all of the processes impacting the time-averaged particle nitrate concentration, including oxidation of NO<sub>x</sub> and SO<sub>2</sub>, thermodynamic equilibrium, and deposition.

We focus our analysis on winter conditions, when nitrate is most important, and in the Eastern United States, where the large sulfate concentrations add additional complexity. We use a variety of modeling tools and observational datasets to examine the inorganic aerosol system and to investigate the robustness of our candidate indicators.

### 1.2. Modeling tools

We use two models to explore the sensitivity of the inorganic aerosol system to changes in emissions and changes in precursor concentrations.

To examine the sensitivity of the aerosol concentrations to emissions, it is necessary to model the transport, chemical transformation of emitted species, and deposition, as well as aerosol thermodynamics. For this task, we use the Community Multiscale Air Quality (CMAQ) model. The inputs to CMAQ are the emissions and meteorological conditions and the outputs are the aerosol and gas-phase concentrations in a three-dimensional Eulerian grid. A complete description of the CMAQ modeling system used in this study can be found in the second part of this series (Dennis et al., [this issue](#)). For most of the analysis, we focus on 14 locations: 10 urban grid cells selected because they span the range of chemical conditions typically found in the Eastern United States during winter, and four rural sites selected because they have  $DSN < 1.5$ . The details of these locations and a map of the modeling domain are included in Supplemental Information.

To analyze the aerosol under equilibrium conditions, we use the Aerosol Inorganics Model (AIM) (Clegg et al., 1998; Wexler and Clegg, 2002). AIM is a process model that performs a Gibbs free energy minimization to calculate the equilibrium aerosol concentration given the temperature, relative humidity, and aerosol precursor concentrations in a confined volume. AIM allows us to investigate in detail the sensitivities under equilibrium conditions.

We make a few simplifying assumptions in the AIM equilibrium calculations. We do not model the influence of minor ions ( $Ca^{2+}$ ,  $Na^+$ ,  $Cl^-$ ) because their concentrations are low relative to  $SO_4^{2-}$ ,  $NO_3^-$ , and  $NH_4^+$  in polluted airsheds (Christoforou et al., 2000). We assume that the aerosol is always in the aqueous phase, which is consistent with winter observations in the Eastern United States (Rood et al., 1989; Takahama et al., 2004). Finally, we model only the mass found in particles with

diameter  $< 2.5 \mu m$  ( $PM_{2.5}$ ). This assumes that the equilibrium concentration is not influenced by the composition of larger particles. Previous studies have shown that while the fine particles are found in equilibrium with the gas-phase concentrations, this may not be true for coarse particles due to slower mass transfer (Meng and Seinfeld, 1996).

### 1.3. Observational datasets

In addition to modeling tools, we use measurements of  $SO_4^{2-}$ ,  $NO_3^-$ ,  $NH_4^+$ , TN, and TA from the Pittsburgh Air Quality Study (PAQS), part of the EPA PM Supersites program. These measurements were made on a continuous basis using the steam sampler of Khlystov et al. (1995), and then averaged to hourly or two-hourly values. The site is located at 40.4395 N latitude, 79.9405 W longitude, approximately 6 km east of downtown Pittsburgh (Wittig et al., 2004).

## 2. Candidate indicators

Previously, Ansari and Pandis (1998) developed the gas ratio (GR) as an indicator of the sensitivity of particle nitrate to a change in TA or TN concentration. The GR is defined as the ratio of free ammonia to total nitrate:

$$GR = \frac{\text{free ammonia}}{\text{total nitrate}} = \frac{TA - 2 \times TS}{TN}. \quad (2)$$

The free ammonia is the ammonia that is available to form ammonium nitrate in the equilibrium processes. An implicit assumption of the GR is that the sulfate is fully neutralized, such that two times the moles of sulfate are unavailable to form ammonium nitrate.

When there is an abundance of free ammonia ( $GR > 1$ ), most of the TN is in the particle phase and much of the TA is in the gas phase. Under these conditions, the particle nitrate concentration is most sensitive to changes in the TN. Alternatively, when there is an abundance of TN ( $GR < 1$ ), the particle nitrate concentration is most sensitive to changes in ammonia.

Similarly, Blanchard et al. (2000) have proposed the excess ammonia (EA) indicator, defined as

$$EA = TA - 2 \times TS - TN - [HCl(g)] + 2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+] - [Cl^-]. \quad (3)$$

This formulation is similar to the GR, except that it also includes minor ions. It also differs from the

GR in that it is a difference of the anions and cations, rather than a ratio. However, without the minor ions, the EA can be expressed as a function of the GR and TN with no additional information. Therefore, we do not include EA among our candidate indicators.

When calculating the free ammonia, both the GR and EA assume that the sulfate is fully neutralized by ammonium, or  $DSN = 2$ . However, the strong thermodynamic affinity between ammonium and nitrate at cooler temperatures causes ammonium nitrate to be present when the sulfate is not fully neutralized. In Fig. 1, we have used the thermodynamic equilibrium model AIM to calculate the particle composition and DSN over a range of TA concentrations for common winter conditions in the Eastern United States ( $T = 265$  K). Particle nitrate is present even though the sulfate is not fully neutralized. This figure can be contrasted with Fig. 9.23 from Seinfeld and Pandis (1998) where, under warmer conditions (298 K), minimal nitrate formation occurs until the sulfate is fully neutralized. Hence, the common assumption that full

sulfate neutralization precedes ammonium nitrate formation is reasonable for warmer conditions, but may not always apply in the winter. Ambient measurements from the Speciation Trends Network (Chu, 2003) and previous regional scale air-quality modeling (Mathur and Dennis, 2003) have also demonstrated the presence of particle nitrate without full sulfate neutralization under winter conditions. By assuming full neutralization, the GR and EA may underestimate the quantity of free ammonia that is available for particle nitrate formation.

In order to more accurately represent the quantity of free ammonia, we “adjust” the previous formulation of the GR by multiplying the TS by the DSN rather than assuming the sulfate is fully neutralized. Hence, we propose an alternative indicator, the adjusted GR (AdjGR), defined as

$$\begin{aligned} \text{AdjGR} &= \frac{\text{free ammonia}}{\text{total nitrate}} = \frac{\text{TA} - \text{DSN} \times \text{TS}}{\text{TN}} \\ &= \frac{[\text{NH}_3](\text{mol}) + [\text{NO}_3^-](\text{mol})}{[\text{HNO}_3](\text{mol}) + [\text{NO}_3^-](\text{mol})}. \end{aligned} \quad (4)$$

Using the DSN, we are able to extend the GR of Ansari and Pandis (1998) to conditions where the sulfate is not fully neutralized.

We examine the accuracy of these candidate indicators (GR and AdjGR) for their ability to predict the change in particle nitrate given a change in emissions. The GR and EA have been shown to be accurate indicators of the change in particle nitrate at *equilibrium* given a change in total ammonia or total nitrate *concentrations*. Our analysis differs in two ways. First, we are interested in the response to *emission* changes, rather than total ammonia or total nitrate *concentration* changes. Second, we are interested in the change in *time-averaged* concentrations, rather than the *instantaneous equilibrium* concentration. In the following sections, we examine the conditions necessary for applying these observation-based indicators to time-averaged emission sensitivity studies and then examine the accuracy of these indicators when those conditions are met.

### 3. Necessary conditions

Our goal is to evaluate the GR and AdjGR as indicators of the sensitivity of the time-averaged nitrate  $\text{PM}_{2.5}$  to changes in emissions of  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$ . This is a challenge because these indicators are based on thermodynamic equilibrium theory, yet many processes other than aerosol

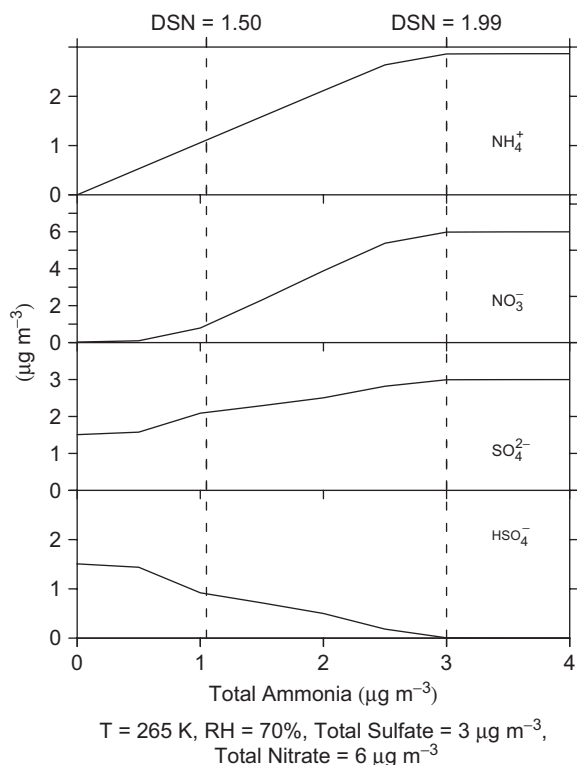


Fig. 1. AIM modeled particle composition for a range of total ammonia concentrations. For a range of conditions, particle  $\text{NO}_3^-$  is present and  $DSN < 2$ .

thermodynamics (such as deposition, advection, dispersion, gas-phase chemistry, and heterogeneous processes) affect the nitrate concentration when averaged over time. First, the time-averaged particle nitrate concentration may diverge from the nitrate concentration that is in equilibrium with the time-averaged ambient concentrations, temperature, and relative humidity. Second, a reduction in emissions does not correspond to a fixed reduction in the TS, TN, and TA. Due to processes other than aerosol thermodynamic equilibrium, the impact of emission controls on the TS, TN, and TA may vary significantly across the domain. This is important because if several locations have the same indicator value yet an emission change yields substantially different TS, TN, and TA concentrations, then the indicator predictions of particle nitrate will have significant error. Therefore, in order for the GR or AdjGR to serve as reliable indicators, these two conditions must hold:

- (i) The time-averaged nitrate concentration is near the thermodynamic equilibrium determined from the time-averaged TS, TN, TA, relative humidity, and temperature.
- (ii) If the changes in TS, TN, and TA due to a fixed change in  $\text{SO}_2$ ,  $\text{NO}_x$ , or  $\text{NH}_3$  emissions vary substantially across the domain, most of that variability must be governed by aerosol thermodynamic equilibrium.

These two conditions are described and tested below.

### 3.1. Time-averaging

Regarding the first necessary condition, if the time-averaged particle nitrate is approximately equal to thermodynamic equilibrium governed by the time-averaged total nitrate, total ammonia, sulfate, relative humidity, and temperature, then we would expect the GR to also be predictive for time-averaged inputs, since the GR has been shown to be predictive for equilibrium conditions (Ansari and Pandis, 1998). A linear function has the property that the average output value is equal to the function applied to the average of each input. However, conventional wisdom suggests that the time-averaged nitrate concentration would not meet this condition, because the equilibrium particle nitrate concentration ( $\text{PM}_{\text{NO}_3}$ ) cannot be described with a linear function of TS, TN, TA, temperature ( $T$ ), and relative

humidity (RH) (West et al., 1999). In this section, we use observations and modeling results to determine if this conventional wisdom is accurate for the wintertime Eastern United States.

First, we compare the 24-h and monthly averaged particle nitrate from PAQS observations and from CMAQ model results to the equilibrium concentrations calculated using AIM. Using the CMAQ outputs and PAQS observations, we calculate the time-average of the TS, TN, TA,  $T$ , RH, either the free ammonia or  $\text{H}^+$  ion concentration, temperature, and relative humidity. These are used as input to AIM, which calculates the equilibrium aerosol concentrations of sulfate, nitrate, and ammonium. In Fig. 2, we compare the time-averaged sulfate, nitrate, and ammonium  $\text{PM}_{2.5}$  with the equilibrium values as predicted by AIM.

Despite the non-linear nature of the thermodynamic equilibrium and the many other competing processes, the daily and monthly average particle concentrations are close to thermodynamic equilibrium. One explanation is that the relationship between the aerosol nitrate partitioning and the TS, TN, TA,  $T$ , and RH is approximately linear over the domain of concentrations and conditions relevant to the Eastern United States in the winter, because a linear function has the property that the time-averaged output can be accurately calculated from the time-averaged inputs. To test this explanation, we assume the equilibrium function is linear and of the form

$$\text{PM}_{\text{NO}_3} = p_0 + p_1\text{TS} + p_2\text{TA} + p_3\text{TN} + p_4T + p_5\text{RH} + \varepsilon. \quad (5)$$

We estimate the coefficients,  $p_0$ – $p_5$ , using linear regression with two datasets: semi-continuous PAQS observations and instantaneous hourly model predictions from CMAQ. If there exists a set of coefficients, such that  $\varepsilon \ll \text{PM}_{\text{NO}_3}$ , then the equilibrium relationship can be approximated as a linear function.

It is important to note that we are not testing if the equilibrium particle nitrate concentration relationship is linear *in general*. Instead, we are testing if it can be approximated as a linear function for the range of concentrations and conditions found at a specific location. The regression coefficients should not be used to calculate the  $\text{PM}_{2.5}$  nitrate for other locations or even these locations during different time periods. Our goal instead is to explain why the equilibrium particle nitrate concentration calculated

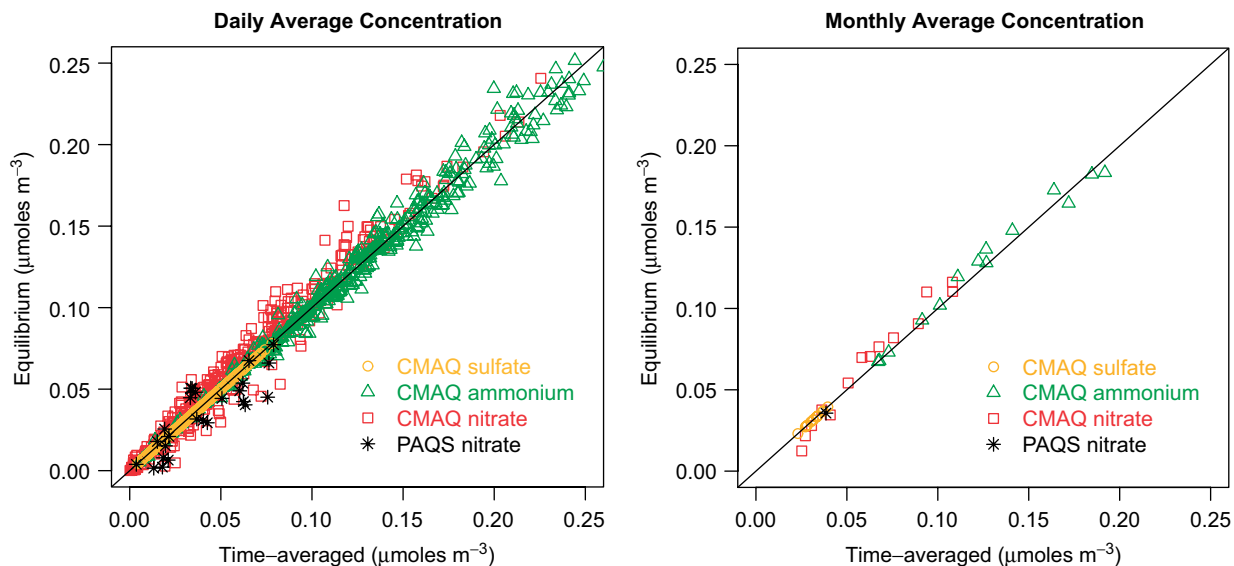


Fig. 2. Comparison of AIM calculated equilibrium concentration and time-averaged particle sulfate, nitrate, and ammonium from CMAQ and particle nitrate from PAQS for January 2002. CMAQ values are from 14 representative locations listed in Supplemental Information.

using time-averaged concentrations and conditions is approximately equal to the time-averaged  $\text{PM}_{2.5}$  nitrate concentration.

In Fig. 3, we compare these linear model predicted values with the 2-h averaged PAQS observations and CMAQ model results at Pittsburgh during January 2002 and July 2001. In January, the equilibrium function can be reasonably approximated using a linear function. To demonstrate that this phenomenon is not unique to Pittsburgh, we repeat the linear model estimation using CMAQ outputs from 14 sites across the Eastern United States, ranging in GR from 0.06 to 2.69. The results for New York City and a grid cell with both low DSN and high particle nitrate concentrations (labeled X1) are shown in Fig. 3; the other sites can be found in Supplemental Information.

At locations where  $\text{DSN} > 1.5$ , the linear regression model has low error during winter. In both seasons, the largest error is encountered when the total ammonia is far less than what is necessary to neutralize the sulfate concentration. The competition between the nitrate and sulfate for the scarce ammonia is highly dependent on the temperature, relative humidity, and sulfate concentration. In this regime, small changes in the sulfate cause large changes in the free ammonia, which causes non-linear changes in the equilibrium particle nitrate concentration.

In the summer in the Eastern United States, PAQS observations, the Speciation Trends Network observations (Chu, 2003), and previous modeling studies (Mathur and Dennis, 2003) suggest that the sulfate is more abundant and often cannot be fully neutralized by the total ammonia. Under these conditions, the nitrate concentrations are very low, difficult to predict, and non-linear with respect to the TS, TN, and TA concentrations (see lower-left and lower-middle panels in Fig. 3).

In the winter in the Eastern United States, the linear regression model has low error not because the system is completely linear, but because for a given location, the range of concentrations and conditions is limited and the system can be approximated as linear over that narrow range. The concentrations of TS, TN, and TA are often equally abundant (Sickles, 1999). In the CMAQ modeling results at each location, the GR generally does not vary outside of a narrow range around the mean. At low DSN, the system becomes so unstable that even over a narrow range of conditions, the relationship can no longer be approximated as linear (see lower-right panel in Fig. 3). However, these low sulfate neutralization conditions are rare in the winter observations and simulations.

For most winter conditions, the equilibrium particle nitrate concentration can be approximated using a linear function. Therefore, the time-averaged particle nitrate concentration can be estimated

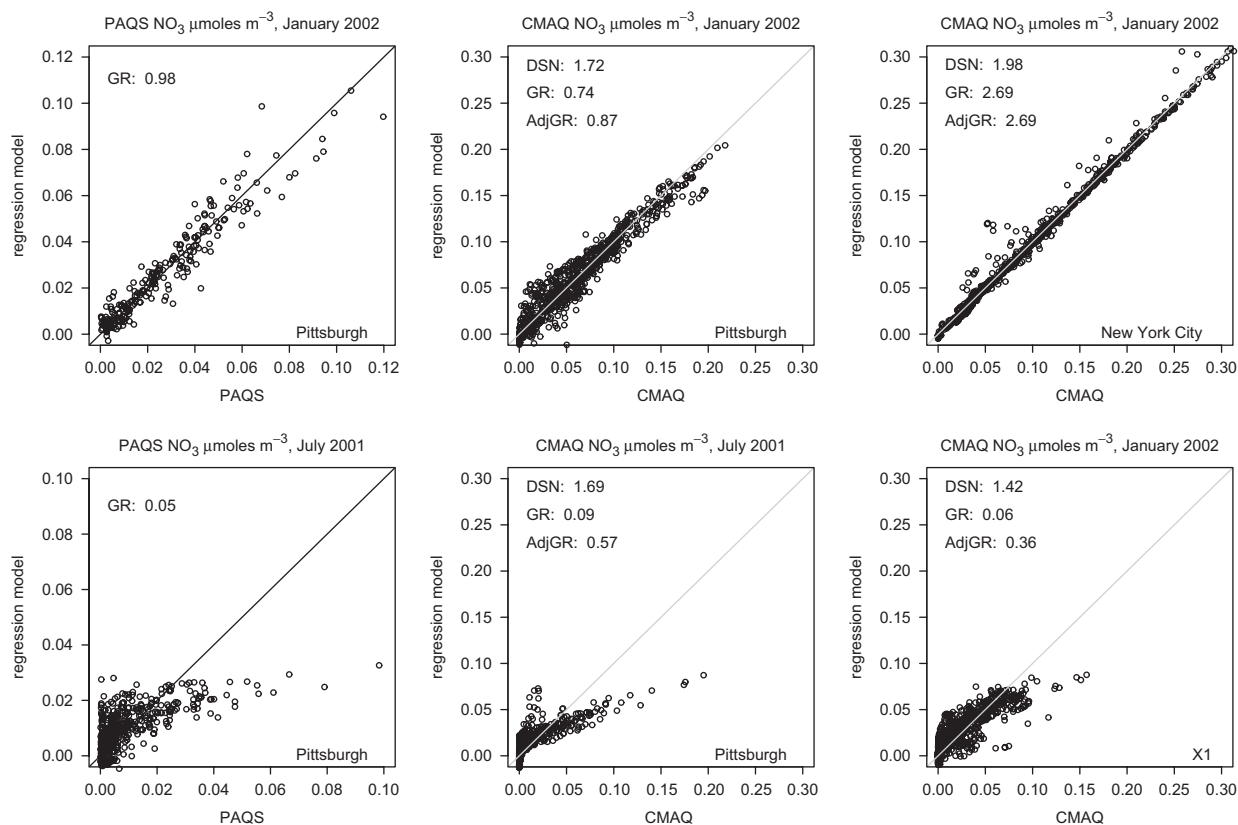


Fig. 3. A linear model to predict the hourly particle nitrate concentration from TA, TN, and TS concentrations, temperature, and RH. In January, both the CTM modeled (CMAQ Pittsburgh grid cell) and observed (PAQS) particle nitrate can be estimated using a linear model. Regression coefficients and  $r^2$  values can be found in Supplemental Information. The January analysis is repeated using CMAQ results from New York City and a location with low DSN (X1) to illustrate that this phenomenon is not unique to Pittsburgh.

from the time-averaged TS, TN, and TA concentrations, temperature, and relative humidity. The equilibrium concepts of GR and AdjGR are applicable as indicators for the time-averaged particle nitrate concentration.

### 3.2. Emission sensitivity

The second necessary condition requires that our candidate indicators can explain most of the spatial variability in the sensitivity of ambient concentrations (TS, TN, and TA) to a change in emissions ( $\text{SO}_2$ ,  $\text{NO}_x$ , or  $\text{NH}_3$ ). The previous section demonstrated that the equilibrium-based candidate indicators can explain the change in particle nitrate due to a change in the time-averaged TS, TN, and TA. However, the complex chemical oxidation processes that convert  $\text{NO}_x$  to nitric acid and  $\text{SO}_2$  to sulfate are not governed by aerosol thermodynamic equilibrium, and therefore may not be captured by our

candidate indicators. It is important to determine for the spatial and temporal domain of interest: is the variability in these oxidation processes, and hence the variability in the conversion of  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$ , to TS, TN, and TA, small compared to the variability explained by our candidate indicators?

To answer this question, we use CMAQ to simulate the change in monthly average TS, TN, and TA concentrations for three cases: a 25% reduction in  $\text{SO}_2$ , a 30% reduction in  $\text{NO}_x$ , and a 20% reduction in  $\text{NH}_3$  emissions. Emission reductions are applied as a constant factor to all sources at all times, hence any variability in the response is due to variability in the chemical and physical processes at different locations in the domain. To ensure regulatory relevance, times and locations where the sum of particle sulfate, nitrate, and ammonium is  $< 5 \mu\text{g m}^{-3}$  are excluded from the analysis. The CMAQ simulated surface concentra-

tions in each grid cell are averaged for January 2002, and the ratio of the change in the TS, TN, and TA concentrations to the change in emissions is shown in Fig. 4. For example, a value of  $-1.0$  corresponds to a 20% reduction in concentration for a 20% reduction in emissions, and a value of  $+0.5$  corresponds to a 10% increase in concentration for a 20% reduction in emissions. The box plot denotes the spatial distribution of the change in monthly average TS, TN, and TA concentrations, where the dark line within each “box” is the median change. The upper and lower bounds of each box mark the 25th and 75th percentile, and the whiskers denote the 5th and 95th percentile. Therefore, the distance from zero corresponds to the impact each emission change has on the precursors, and the range of the whiskers denote the variability of the change across the modeling domain.

The spatial variability in the decrease of TS due to a decrease in  $\text{SO}_2$  emissions can be explained by differences in the extent to which sulfate production is limited by  $\text{SO}_2$  or limited by the availability of oxidants. However, this variability is small. In addition, the changes in TA and TN due to an  $\text{SO}_2$  emission reduction are negligible.

A reduction in  $\text{NO}_x$  emissions causes a significant increase in the TS and a highly variable decrease in the TN. Using the sulfate-tracking version of CMAQ, we find that a decrease in  $\text{NO}_x$  emissions increases the winter oxidant concentrations, which increases the rate of  $\text{SO}_2$  to  $\text{SO}_4^{2-}$  conversion. Also, the decrease in nitric acid causes an increase in the pH dependent pathways for aqueous-phase sulfate production. Furthermore, the change in TN for a

fixed change in  $\text{NO}_x$  emissions is highly variable across the Eastern United States and also dependent on oxidant concentrations. The impacts of these changes on the gas-phase and aqueous chemistry are not correlated with the ratio of free ammonia to total nitrate, therefore we expect significant error in the relationship between our candidate indicators and the changes in particle nitrate resulting from a  $\text{NO}_x$  emissions reduction.

The decrease in  $\text{NH}_3$  emissions causes a significant decrease in TN and TA. Also, the TN decrease has significant variability. However, the variability in the TN reduction is directly related to the ratio of the free ammonia to total nitrate. A reduction in TA causes more of the TN to be in the gas phase. The gas-phase nitric acid has a much higher deposition rate compared to the particle phase, which causes a decrease in the TN budget. As shown in the following section, the change in TN due to  $\text{NH}_3$  emission reduction is well correlated with the GR and AdjGR, hence the amount of variability explained by our candidate indicators is substantial. The decrease in  $\text{NH}_3$  emissions does have a minor impact on the TS. Use of the sulfate-tracking version of CMAQ suggests that this reduction is due to a decrease in the pH of the cloud droplets. However, the spatial variability of this impact is small so it should have little effect on the relationship between our candidate indicators and the changes in nitrate due to  $\text{NH}_3$  emissions reductions.

### 3.3. Summary of necessary conditions

Two important pre-conditions are necessary for the use of the AdjGR and GR as indicators for the nitrate response to emission controls. First, the monthly average nitrate concentrations must be approximately equal to the equilibrium concentrations calculated from the monthly average TS, TN, and TA concentrations, temperature, and relative humidity. This condition is satisfied during winter at most locations in the Eastern United States. However, when the  $\text{DSN} < 1.5$  (rarely in the winter, frequently in the summer), the equilibrium function is highly non-linear and this condition no longer holds. Second, if the change in the TS, TN, and TA due to a fixed change in  $\text{SO}_2$ ,  $\text{NO}_x$ , or  $\text{NH}_3$  emissions varies substantially across the domain, that variability must be governed by thermodynamic equilibrium processes. This condition is met for  $\text{SO}_2$  and  $\text{NH}_3$  emission changes during winter, but not for  $\text{NO}_x$ .

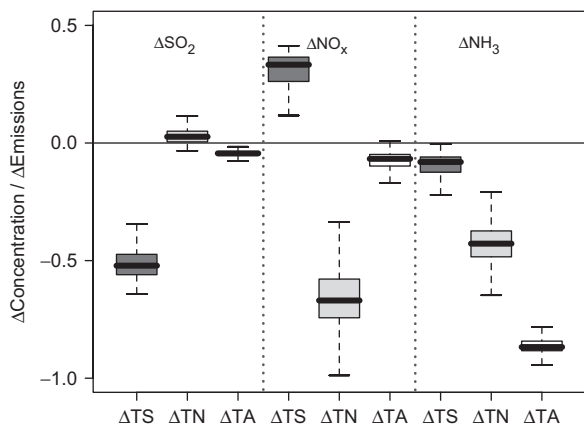


Fig. 4. Sensitivity of TS, TN, and TA to change in emissions of  $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$  as predicted by CMAQ simulation of January 2002.



#### 4. Evaluation of indicator accuracy

Given that these criteria in Section 3 have been satisfied for SO<sub>2</sub> and NH<sub>3</sub> emission reductions, we now develop a functional form that relates the AdjGR and GR to the change in nitrate concentration due to an emission reduction. Using the CMAQ results, we calculate the monthly average AdjGR, GR, and particle nitrate. We then complete three additional CMAQ simulations, each with a reduction in either SO<sub>2</sub>, NO<sub>x</sub>, or NH<sub>3</sub> emissions. The nitrate relative response (RR) is calculated as the percent change in the monthly average PM<sub>2.5</sub> nitrate concentration from the base simulation to the emissions reduction case (Eq. (6)). We restrict our analysis to polluted grid cells with > 5 μg m<sup>-3</sup> of inorganic PM<sub>2.5</sub> (SO<sub>4</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup> + NH<sub>4</sub><sup>+</sup>), as those are most relevant to air-quality management:

$$\text{Nitrate RR} = \frac{[\text{NO}_3^-]_{\Delta\text{emis}} - [\text{NO}_3^-]_{\text{base}}}{[\text{NO}_3^-]_{\text{base}}} \times 100 \quad (6)$$

With these CMAQ simulated values of the monthly average AdjGR, GR, and nitrate RR, we fit a three-parameter sigmoid function that relates the candidate indicator to the nitrate RR (Eq. (7), “log” refers to the natural logarithm). To estimate the parameters, we use the drc package (Ritz and Streibig, 2005) from the R statistical software project. The S-shaped sigmoid function is appropriate since the inorganic aerosol system is essentially an acid-base titration. The best-fit parameters are shown in Table 1:

$$\text{Nitrate RR} = \frac{p_2}{1 + \exp(p_1 \log x - \log p_3)}, \quad x \in \{\text{AdjGR, GR, } \dots\}. \quad (7)$$

To evaluate our candidate indicators, it is appropriate to compare them to the Nitrate RR computed by CMAQ. The gray points in Fig. 5 plot the CMAQ-predicted nitrate RR against the candidate indicators for a change in SO<sub>2</sub>, NO<sub>x</sub>, and NH<sub>3</sub> emissions. The solid line is the best-fit parameterization (Eq. (7)) relating the candidate indicators to the nitrate RR. The mean difference between the CMAQ-predicted nitrate RR and the indicator-predicted nitrate RR (the solid line) is shown in Table 2. For changes in SO<sub>2</sub> and NH<sub>3</sub> emissions, both indicators are nearly unbiased, as the mean difference is close to zero. The parameters in Table 1 are germane to the specific domain, time period, and emission reduction strategy. For a different time period, location, or emission change, it is important

Table 1

Best-fit parameters for sigmoid function (Eq. (7)) relating nitrate RR to the candidate indicators for a change in SO<sub>2</sub> or NH<sub>3</sub> emissions

Names	Estimate	S.E.	<i>t</i> Value	<i>Pr</i> ( <i>x</i> >   <i>t</i>  )
AdjGR ΔSO <sub>2</sub>				
<i>p</i> <sub>1</sub>	2.745630	0.0749	36.6	<2e-16
<i>p</i> <sub>2</sub>	14.891931	0.391	38.1	<2e-16
<i>p</i> <sub>3</sub>	0.587996	0.0132	44.2	<2e-16
GR ΔSO <sub>2</sub>				
<i>p</i> <sub>1</sub>	2.6407818	0.0628	42.0	<2e-16
<i>p</i> <sub>2</sub>	11.7544837	0.147	79.9	<2e-16
<i>p</i> <sub>3</sub>	0.6164712	0.00839	73.5	<2e-16
AdjGR ΔNH <sub>3</sub>				
<i>p</i> <sub>1</sub>	1.680657	0.0360	46.6	<2e-16
<i>p</i> <sub>2</sub>	38.878232	0.544	71.4	<2e-16
<i>p</i> <sub>3</sub>	0.982989	0.0188	52.1	<2e-16
GR ΔNH <sub>3</sub>				
<i>p</i> <sub>1</sub>	1.799139	0.0323	55.7	<2e-16
<i>p</i> <sub>2</sub>	33.383185	0.235	142	<2e-16
<i>p</i> <sub>3</sub>	1.143839	0.0116	98.2	<2e-16

to re-estimate these parameters using a CTM. Due to the impact of NO<sub>x</sub> emissions on oxidation chemistry, neither indicator is a reliable estimator of the nitrate RR for NO<sub>x</sub> emission reductions (see middle panels in Fig. 5); therefore, we do not calculate a best-fit parameterization.

While the indicators have similar performance in aggregate, the AdjGR performs considerably better when the DSN diverges significantly from full neutralization, shown as black x's in Fig. 5. The AdjGR has lower error for these locations since it uses a more accurate representation of the free ammonia by removing the assumption that DSN is 2.

For the case of 25% SO<sub>2</sub> emission reduction, the nitrate RR approximated using the AdjGR is within ±2 absolute RR percentage points of the CMAQ-predicted nitrate RR in 90% of these cases. For example, if the AdjGR-estimated nitrate RR is 6%, then 90% of the time CMAQ would predict a nitrate RR that is between 4% and 8%. For a 20% NH<sub>3</sub> emission reduction, 85% are within this bound. Before applying these indicators, it is important to use a CTM to calculate the magnitude of these uncertainties for the domain and emission reduction scenario of interest.

For these tests, we have selected a simple domain-wide emission reduction of a single pollutant. In

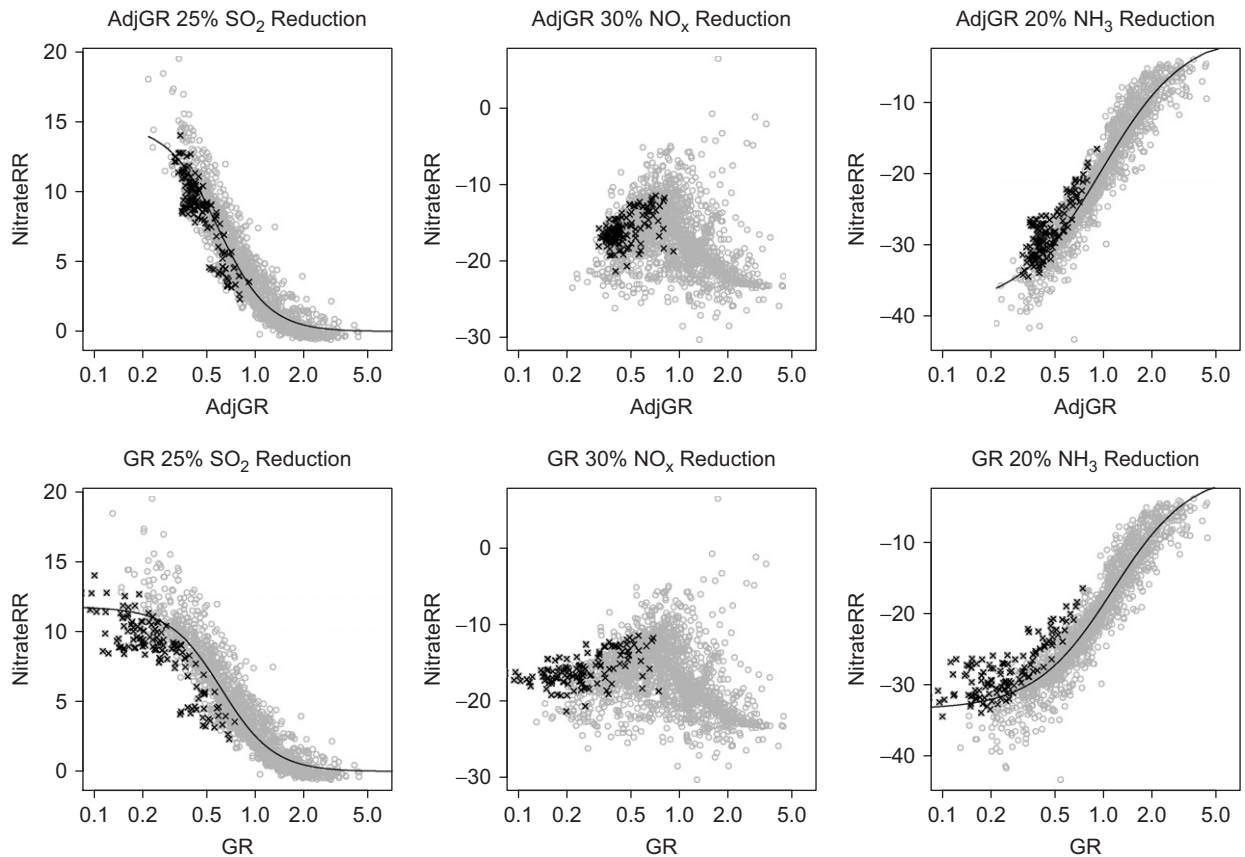


Fig. 5. Monthly average AdjGR, GR, and nitrate RR, where each point represents a CMAQ grid cell, for all cells where the monthly average inorganic  $\text{PM}_{2.5} > 5.0 \mu\text{g m}^{-3}$ . The solid line indicates the best-fit regression model (not shown for  $\text{NO}_x$ ). The black x's denote CMAQ grid cells where the  $\text{DSN} < 1.5$ . The AdjGR substantially improves the error variance for these locations, due to the more accurate representation of the free ammonia. Eleven locations, all with  $\text{DSN} < 1.5$ , have  $\text{GR} < 0.1$  and fall outside of the plotted range.

Table 2

Mean difference, mean absolute difference, and difference variance between CMAQ-predicted nitrate RR ( $C_{\text{nRR}}$ ) and indicator-predicted nitrate RR ( $I_{\text{nRR}}$ ) using the functional fit from Eq. (7)

	Mean ( $C_{\text{nRR}} - I_{\text{nRR}}$ )	Mean ( $ C_{\text{nRR}} - I_{\text{nRR}} $ )	$\sigma^2$ ( $C_{\text{nRR}} - I_{\text{nRR}}$ )
AdjGR $\Delta\text{SO}_2$	9.6E-4	0.94	1.6
GR $\Delta\text{SO}_2$	5.5E-3	0.99	1.9
AdjGR $\Delta\text{NH}_3$	1.6E-2	1.6	4.9
GR $\Delta\text{NH}_3$	2.7E-2	1.8	5.8

reality, emission reduction programs and changes in technology cause simultaneous changes in the spatial and temporal distribution of future emission rates for all three pollutants ( $\text{SO}_2$ ,  $\text{NO}_x$ , and  $\text{NH}_3$ ). The methods we have outlined can be applied to determine the extent to which the AdjGR is a

reliable indicator of the Nitrate RR for a specific future emission scenario.

## 5. Conclusions

We have identified two robust indicators, the AdjGR and GR, for using ambient concentrations to estimate the sensitivity of  $\text{PM}_{2.5}$  nitrate to  $\text{SO}_2$  and  $\text{NH}_3$  emission changes. The AdjGR and GR are based on aerosol equilibrium thermodynamics, but they are useful for predicting the nitrate response to a  $\text{SO}_2$  or  $\text{NH}_3$  emission change because the winter monthly average nitrate concentrations are near equilibrium. Additionally, the  $\text{SO}_2$  and  $\text{NH}_3$  emission changes impact the aerosol precursors TA, TN, and TS in a way that is correlated with the AdjGR and the GR.  $\text{NO}_x$  emission reductions alter the oxidization capacity of the atmosphere, and hence alter the TS and TN concentrations in a

way that cannot be explained using the ratio of free ammonia to total nitrate.

Previous studies have noted that when the free ammonia exceeds the total nitrate, the inorganic aerosol system is more sensitive to reductions in total nitrate than ammonia. However, our use of these indicators allows for a more nuanced evaluation. First, it is possible to estimate the percent change in particle nitrate, not just the relative sensitivities. We find that even in cases when the free ammonia exceeds the total nitrate by a factor of 2, a 20% reduction in  $\text{NH}_3$  emissions yields a 10% reduction in particle nitrate. Thus, the sensitivity to ammonia is not negligible. Second, the impact of ammonia emission reductions are more predictable at a given indicator level, because  $\text{NO}_x$  impacts so many atmospheric processes. At locations over the Eastern United States where the free ammonia is double the total nitrate, the nitrate RR for a 30% reduction in  $\text{NO}_x$  emissions ranges from  $-1\%$  to  $-27\%$ .

The choice of indicator should be governed by practical considerations important to the domain of interest. The AdjGR requires measurements of gas-phase ammonia, particle nitrate, and gas-phase nitric acid. The GR only requires measurements of the total nitrate, the total ammonia, and sulfate. Although the AdjGR is more accurate where  $\text{DSN} < 2$ , the accuracy of the two methods converges as the DSN approaches 2.

As noted in the previous section, the nitrate RR calculated from the AdjGR has an uncertainty of  $\pm 2$  absolute RR percentage points for a 25% reduction in  $\text{SO}_2$  or a 20% reduction in  $\text{NH}_3$ . This uncertainty exists because the ratio of the free ammonia to total nitrate does not capture all of the processes that control the particle nitrate concentration. The advantage of using the AdjGR is that it is based on observations germane to a specific location. While CMAQ has a more complete description of relevant processes, it is limited by errors in the emission inventory and meteorological inputs. These input errors cause errors in the spatial distributions of free ammonia and total nitrate and therefore cause errors in the nitrate RR predictions at a given location. These two approaches, observable indicators and emissions-based modeling, have largely independent sources of error. Therefore, both should be used in a complementary manner to assess the effectiveness of emission control scenarios. We have shown that the air-quality model can provide the relationship between

the AdjGR and the nitrate response to a particular emission control scenario for a given domain and time period. Then the AdjGR, measured at specific locations, can be used to predict the change in particle nitrate due to the specific emission reduction strategy as simulated in the air-quality model. Using a combination of air-quality models and reduced-form functions based on indicators and observations, it is possible to more accurately estimate the effectiveness of emission control scenarios.

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### Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.atmosenv.2007.10.039](https://doi.org/10.1016/j.atmosenv.2007.10.039).

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