Diagnostic Evaluation of CMAQ Response of Inorganic Fine Particulate Species to Emissions Changes

Robin L. Dennis[+], Shawn J. Roselle[+], Prakash V. Bhave[+]

Atmospheric Sciences Modeling Division
Air Resources Laboratory
National Oceanic and Atmospheric Administration
Research Triangle Park, NC 27711

[+] On Assignment to the National Exposure Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park

Abstract

Introduction
A critical use of regional air quality models is to predict changes in particulate mass associated with changes in emissions. However, it is known that the inorganic fine particle system's response can be nonlinear. One aspect of its nonlinearity is that nitrate can replace sulfate when SO_2 emissions are decreased. Complex models are needed to be able to simulate these nonlinearities to estimate the response to emissions reductions. It would be very useful if we could identify diagnostic indicators of the sensitivity of the inorganic system to changes in the state of the atmospheric system. We could then use these indicators to test attributes of the fine particulate models' predictions and address prediction uncertainty.

The Gas Ratio, proposed by Spyros Pandis and his colleagues, has potential for being such an indicator.

$$\text{Gas Ratio (GR)} = \frac{\text{Free Ammonia}}{\text{Total Nitrate}} = \frac{NHx_{(moles)} - 2*SO4_{(moles)}}{\text{Total-Nitrate}_{(moles)}}$$

The Gas Ratio identifies whether the system is nitric acid (total nitrate) or ammonia (total ammonia) limited. It may be an indicator of the sensitivity of the inorganic system to changes in system state.

If GR is < 1, then the system is ammonia-limited. The amount of aerosol nitrate formed is limited by lack a ammonia. One expects that the release of ammonia due to a reduction in sulfate will result in an increase in aerosol nitrate.

If GR is > 1, then the system is nitric acid limited and most of the budget is partitioned to aerosol nitrate. The amount of aerosol nitrate formed is limited by the availability of nitric acid. One expects that the release of ammonia due to a reduction in sulfate will have little effect on levels of aerosol nitrate.

A CMAQ sensitivity study was designed to examine the Gas Ratio and assess its capability to be used as an indicator. The system response of interest was the degree to which nitrate replaces sulfate as sulfate is reduced. This is a question of great interest to the regulatory community. Two broad questions were addressed in the initial study:

(1st): Is the Gas Ratio a precise indicator of system response (more quantitative) or a more general indicator of system response (more qualitative)?

Corollary: can we characterize that system response in a manner useful to air quality managers?

(2nd): As a ratio, there is also the issue that a model can get the correct ratio for the wrong reason or get the correct ratio for the right reason. Does it make a difference whether we get the Gas Ratio for the right reason. Is it sufficient just to get the correct Gas Ratio?

To answer the first question, two sensitivities were designed:

* S-1: Assess the change in the nitrate mass, due to replacement, in response to differences in total-nitrate (tot-NO$_3$) available ($\pm$ total-NO$_3$).
* S-2: Assess the change in the nitrate mass, due to replacement, in response to differences in total-ammonia (NH$_X$) available ($\pm$ NH$_X$).

We desired simulations close to GR = 1 as a starting point to see what happens as we move to either side of GR = 1. The reduction in sulfate to be as similar as feasible across the sensitivities. To answer the second question, a third sensitivity was designed:

* S-3: Create approximately equal changes in total-nitrate and total-ammonia to create a Gas Ratio as close to the original Gas Ratio as feasible and compare the two predictions of the change of nitrate, due to replacement.

We started with the winter period when nitrate is highest and when sulfate is expected to be more fully neutralized. We first looked at Pittsburgh for January 2002. Data exists to define the observed GR and the GR was centered around 1. Also, the CMAQ-simulated GR was close to the observed GR, although for the wrong reason (both total-NO$_3$ and NH$_X$ were biased high). We used daily means, the longest averaging time possible before losing accuracy of interpretation.

Results for S-1 ($\pm$ total-NO$_3$): Reducing (increasing) total-NO$_3$ increased (decreased) the GR, as expected. The magnitude of the absolute increase in aerosol nitrate due to the reduction of sulfate does down with the higher GR and vice versa. The relative increase in aerosol nitrate does not change as the GR changes. Thus, the relative reduction factor for the increase in aerosol nitrate is not sensitive to bias or error in the total-NO$_3$.

Results for S-2 ($\pm$ NH$_X$): Reducing (increasing) NH$_3$ emissions decreases (increases) the GR, as expected. The magnitude of the absolute increase in aerosol nitrate due to the reduction of sulfate basically does not change as the GR changes. The relative increase in aerosol nitrate increases as the GR decreases and decreases as the GR increases. Thus, the relative reduction factor for the increase in aerosol nitrate is sensitive to bias or error in NH$_X$.

Results for S-3 (same GR): For the GR with the lower NH$_X$, the relative increase in aerosol nitrate, due to replacement, is higher, similar to what occurred in S-2. Thus, the relative reduction factor for two equal Gas Ratios is not the same. The change in NH$_X$ appears to be controlling the behavior of the relative reduction factor.

CMAQ with ISORROPIA indicates that there is a 1 mole increase in nitrate per mole decrease in sulfate. The preliminary explanation for these results is that, while the "dry" model of aerosols

informs most conceptual models, the liquid model which is more correct for conditions across the eastern U.S. gives a different answer. In the liquid model the In the liquid model the NH_4^+ and NO_3^- do not condense/evaporate in equimolar quantities. Rather, they respond to changes in the aerosol acidity. However, NO_3 partitioning appears to be less sensitive to pH than NH_X partitioning for the range of pH encountered in Pittsburgh in January 2002.

The Gas Ratio is not a black-and-white indicator of the system response to SO_4 decreases. The system response varies smoothly for GR changes around GR=1. Errors in the components of the GR can be related to uncertainty in the relative reduction factors that might be used for aerosol nitrate increases when SO_4 is reduced. A 25% bias in NH_X appears to create roughly a 15-20% bias in the nitrate relative reduction factor. Errors in total-NO_3 appear to create minimal error in the relative reduction factor. The same GR's produced by different conditions do not give the same relative reduction factors for replacement. The GR is a useful construct to guide thinking and inquiry about the system.

For application to control strategies, errors in NH_3 emissions appear to be much more important than errors in production of HNO_3. We are expecting significant changes in SO2 and NOX emissions in the near future due to the CAIR proposals. We expect, therefore, to see an ambient signal in the inorganic fine particle system. To be able to really test models and to track this signal in the inorganic components, we need measurements of total-nitrate and NHX to go along with sulfate measurements. These measurements need to be made daily (every day) and, if possible or feasible, made on an hourly or two-hourly basis. The signal will be hard to discern, due to meteorological variability. Thus, we need the largest reduction feasible. We should not be put off by uncertainties in the models. We need a test of the models with a likelihood of success and we need an empirical test of the efficacy of emissions reductions.