Response of Inorganic PM to Precursor Concentrations

A S I F   S.   A N S A R I   A N D   S P Y R O S   N.   P A N D I S *

Department of Chemical Engineering and Engineering and Public Policy, Carnegie Mellon University, 5000 Forbes Avenue, Pittsburgh, Pennsylvania 15213

An inorganic aerosol equilibrium model is used to investigate the response of inorganic particulate matter (PM) concentrations with respect to the precursor concentrations of sulfuric acid, ammonia, and nitric acid over a range of temperatures and relative humidities. Diagrams showing regions of PM response to precursor concentrations are generated, thus allowing the qualification of assumptions concerning the response of PM to sulfate and overall sensitivity to ammonia and nitric acid availability. The PM concentration level responds nonlinearly to sulfate and shows overall sensitivity to ammonia and nitric acid availability for specific atmospheric conditions and precursor concentrations. The generated diagrams are applied as a means of approximating the PM response to precursor concentrations for two urban polluted areas. In both cases, reductions in ammonia emissions have the most significant impact on the total PM level. However, such a reduction will result in significant increases in atmospheric acidity.

Introduction

Atmospheric particles have adverse effects on human health and directly affect visibility and air quality (*1−3*). To alleviate some of these atmospheric problems, it is desired to control atmospheric particulate matter (PM) concentrations. PM consists of many different types of particles covering a broad range of composition and size and can be categorized into primary and secondary. Primary aerosols include automobile exhaust, sea spray and dust, and are emitted into the atmosphere directly from sources. Secondary aerosols, which generally have diameters, $d_p < 2.5$ μm, are produced in the atmosphere from reactions involving primary or secondary gases.

In many regions, secondary components represent a significant fraction of PM$_{10}$ (particles with $d_p < 10$ μm) or PM$_{2.5}$ ($d_p < 2.5$ μm) (*4−6*). The dominant inorganic secondary aerosol species are sulfates, nitrates, and ammonium salts (*3, 5, 7*). Nitrate has been measured in substantial quantities in both fine and coarse particles (*4, 8*) where it is primarily produced via reaction of nitric acid or N$_2$O$_5$ with NH$_3$, NaCl, or dust (*9*). Sodium and chlorides are present in small quantities in the atmosphere over the continental United States. As a first approximation, the interactions of nitric acid with NaCl and dust particles will be neglected in the present study; the implications of this assumption will be discussed in a subsequent section.

As the sulfate/nitrate/ammonium system is a significant component of PM, our objective is to determine how the PM

concentration behaves with respect to the precursor concentrations of sulfate, total (gas + aerosol) ammonia, and total (gas + aerosol) nitric acid. In analyzing the behavior of PM, it has often been assumed that the PM level responds linearly, [d(PM)/d(sulfate)] = 1.00 or 1.34, with respect to sulfate [all [d(PM)/d(x)] given as mass ratios μg m^{-3}/μg m^{-3})]. This assumption is equivalent to the formation of sulfates [e.g., NH$_4$HSO$_4$, (NH$_4$)$_3$H(SO$_4$)$_2$, (NH$_4$)$_2$SO$_4$] while neglecting additional changes in the remaining PM components (e.g., NH$_4$NO$_3$) because of the sulfate change. In addition, it has been proposed that, for some environments, the PM level may not be sensitive to total ammonia availability and will not respond proportionally to total nitric acid availability (for example, refs *3* and *5*). This in general is valid for specific atmospheric conditions and precursor concentrations. While such assumptions allow easy calculations of PM behavior, their applicability needs to be investigated in detail before being used in cost/benefit analyses for PM controls.

In analyzing the response of PM, we define regions showing the qualitative PM response to precursor concentrations (total ammonia, nitric acid, and sulfate), thus qualifying the assumptions mentioned. When referring to changes in precursor concentrations, we assume that these reductions occur independently of one another (e.g., a reduction in sulfate occurs independently of total ammonia and nitric acid concentrations); the implications of this assumption will be discussed later. With the following analysis, it should be noted that all PM simulations refer to the sulfate/nitrate/ammonium component of PM.

PM Simulations

The equilibrium-based inorganic aerosol model, GFEMN (*10*), is used to determine the partitioning of the inorganic components between the gaseous and aerosol phases. GFEMN calculates aerosol concentrations given the system temperature, relative humidity (rh), and total (gas + aerosol) ammonia, total (gas + aerosol) nitric acid, sulfate, sodium, and total (gas + aerosol) chloride concentrations. For the purposes of the present study, we assume that chemical equilibrium is established rapidly between the volatile gaseous- and aerosol-phase species. In addition, it is assumed that all particles of interest have similar chemical composition (internal mixture assumption). Finally, the analyses presented here are applicable for PM responses based on average conditions and PM concentrations or for instantaneous PM responses to precursor changes.

For all PM simulations, the concentrations of total sulfate, nitric acid (gas + aerosol), and ammonia (gas + aerosol) will be varied from zero to maximum values of 50 μg m^{-3} (12 ppb), 80 μg m^{-3} (30 ppb), and 30 μg m^{-3} (40 ppb), respectively. Such high concentrations have been observed in Riverside/Rubidoux, CA (*5*), Laurel Mt., PA (*11*), and New York City, NY (*12*).

PM Response to Sulfate

The NH$_3$−H$_2$SO$_4$−Water System. The predicted piecewise linear behavior for a system consisting of only ammonia and sulfate (zero total nitric acid) is shown in Figure 1. All sulfate in the system will be in the aerosol phase because of the low vapor pressure of sulfuric acid in the presence of water vapor; the aerosol sulfate must be neutralized by available ammonia resulting in the formation of NH$_4$HSO$_4$, (NH$_4$)$_3$H(SO$_4$)$_2$, and/or (NH$_4$)$_2$SO$_4$, depending on the molar ratio of ammonia to sulfate. Relative humidity (rh) and temperature do not affect the amount of sulfate present and thus, Figure 1 can be

* To whom correspondence should be addressed. Phone: 412-268-3531; fax: 412-268-7139; e-mail: spyros@andrew.cmu.edu.
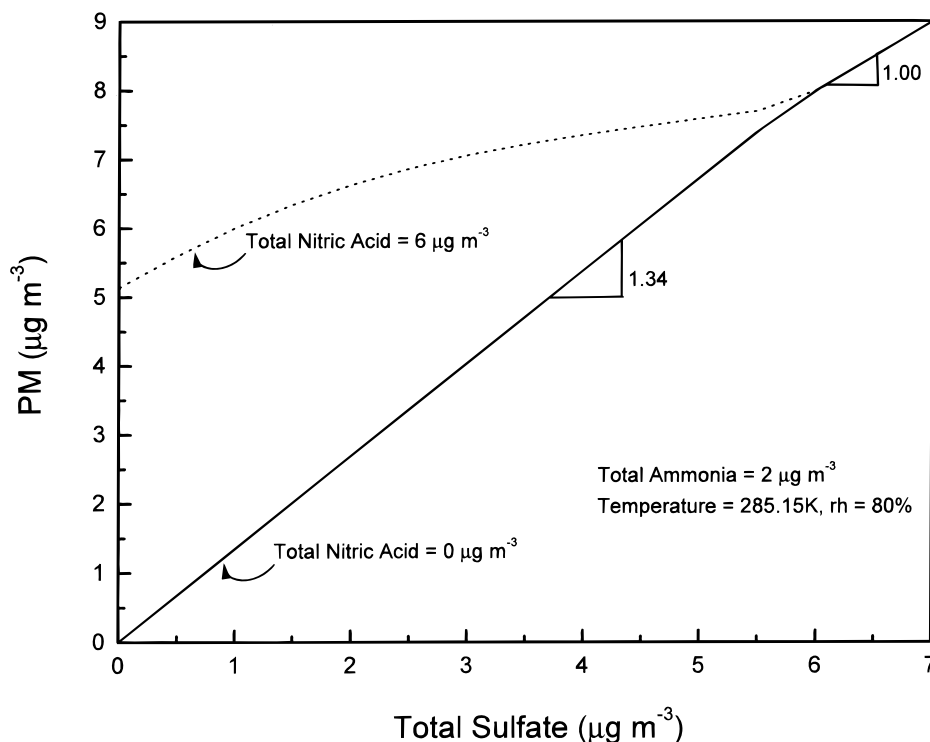
FIGURE 1. PM response to total sulfate for the $NH_3-H_2SO_4$ (total nitric acid = 0 line) and $NH_3-HNO_3-H_2SO_4$ (total nitric acid = 6 μg m^{-3}) systems.

applied to a dry or wet aerosol. As seen, there are two, distinct linear regimes. For cases where the ammonia to sulfate molar ratio is greater than 2 (total sulfate < 6 μg m^{-3}), the PM consists only of $(NH_4)_2SO_4$. In this region, [d(PM)/d(sulfate)] = 1.34. Adding 1 μg of sulfate (0.0102 μmol) to the system causes the formation of 1.34 μg (0.0102 μmol) of $(NH_4)_2SO_4$. For cases where the ammonia to sulfate molar ratio is less than 2, but greater than 1.5, the possible components include $(NH_4)_2SO_4$ and $(NH_4)_3H(SO_4)_2$, and for molar ratios less than 1.5 but greater than 1, the possible components are $(NH_4)_3H(SO_4)_2$ and NH_4HSO_4. In each case, [d(PM)/d(sulfate)] = 1. Cases where the ammonia-to-sulfate ratio is less than 1 result in highly acidic forms of sulfate such as NH_4HSO_4 and H_2SO_4(l). These cases will not be considered further because, in that regime, the PM response to sulfate is linear, [d(PM)/d(sulfate)] = 1.

The $NH_3-HNO_3-H_2SO_4$—Water System. When nitric acid is added to the system discussed in the previous section, the PM response to sulfate becomes more complex (Figure 1). With the addition of nitric acid, for ammonia-to-sulfate molar ratios greater than 2, the components that may exist include NH_4NO_3 and $(NH_4)_2SO_4$. Adding sulfate to the system, regardless of the initial sulfate concentration, will require a specific amount of ammonia for neutralization. The additional sulfate may react with some of the available gas-phase ammonia or, if none is available, with any NH_4NO_3 present. The remaining amount of NH_4NO_3 will be determined by thermodynamic equilibrium. The nonlinearity in the PM behavior results from the behavior of NH_4NO_3 as it is driven by thermodynamic equilibrium between gas and aerosol phases. Hence, if NH_4NO_3 is present, the PM concentration of the system may respond nonlinearly to changes in the total sulfate concentration.

As the presence of NH_4NO_3 indicates a possible nonlinear response of PM to sulfate, atmospheric conditions and precursor concentrations allowing its formation need to be determined before further analysis is conducted. To determine if any NH_4NO_3 is present in a system, the following condition must hold:

$$[NH_3^F][HNO_3^T] > K \qquad (1)$$

where NH_3^F is the free ammonia [total ammonia $-$ (2 $\times$ [sulfate])] and HNO_3^T is the total (gas + aerosol) nitrate concentration (ppb). K (ppb^2) is an equilibrium constant dependent on temperature, rh, and sulfate concentration (13, 14). For low rh, (rh < 55%), NH_4NO_3 and $(NH_4)_2SO_4$ are solid and K is only a function of temperature. The sulfate concentration and rh have no effect on K as the aerosol particles are dry. For high rh (rh > 60%), NH_4NO_3 is in solution and K depends on rh and sulfate concentration in addition to temperature. At high rh, Stelson and Seinfeld (14) examined the influence of sulfate [as $(NH_4)_2SO_4$] on K and determined that, for a particle consisting of 75% NH_4NO_3 and 25% $(NH_4)_2SO_4$ (molar basis), K is lower than that for pure NH_4NO_3 by as much as 40%. However, Stelson and Seinfeld (14) were able to determine the behavior of K with an a priori knowledge of the $(NH_4)_2SO_4$ and NH_4NO_3 concentrations. For our purposes, we wish to determine under which conditions NH_4NO_3 will form given NH_3^F and HNO_3^T without knowing the NH_4NO_3 concentration. Average K will be selected approximating the actual K within 50% for different amounts of $(NH_4)_2SO_4$. These values, calculated with GFEMN, are shown in Table 1. Thus, given the temperature and rh, an appropriate K can be used, and the presence of NH_4NO_3 can be detected with eq 1 indicating a possible nonlinear response of PM to sulfate.

In specifying regions where the PM concentration responds nonlinearly to precursor concentrations, a new parameter is introduced, the gas ratio (GR):

$$GR = \frac{[NH_3^F]}{[HNO_3^T]} \qquad (2)$$

Figure 2 shows [d(PM)/d(sulfate)] as a function of GR calculated by GFEMN for low temperature and rh over a range of HNO_3^T. The curves in Figure 2 are independent of the total sulfate concentration. At a given HNO_3^T, a reduction
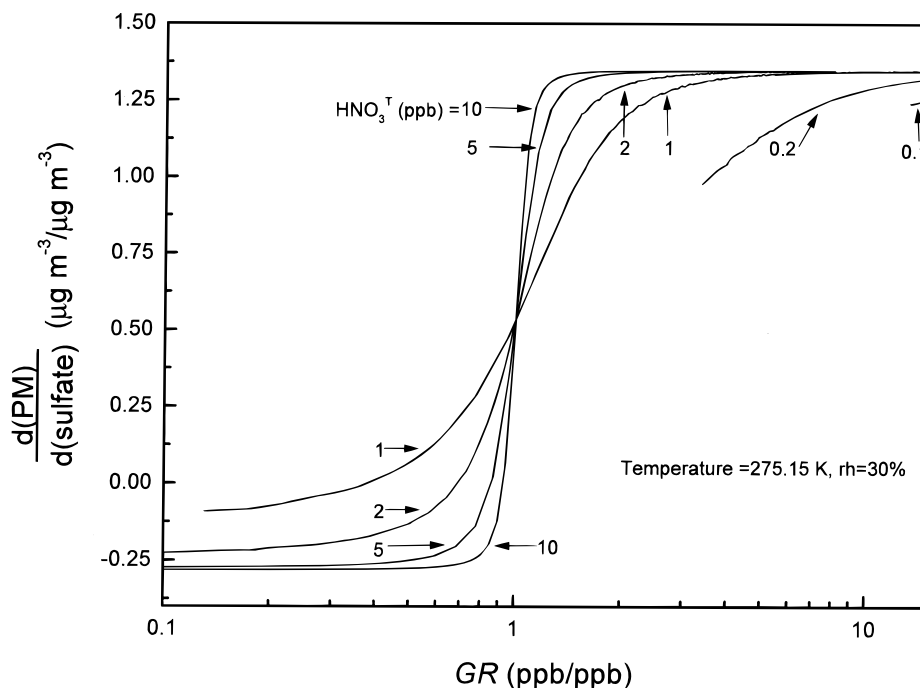
FIGURE 2. [d(PM)/d(sulfate)] as a function of GR for a range of HNO_3^T at low temperatures (275 K) and low rh (30%).

TABLE 1. Equilibrium Constant (K) for a Range of Temperatures and Relative Humidity

temp	K (ppb^2)	
	low rh (30%)	high rh (90%)
low (275 K)	0.13	0.02
moderate (298 K)	45	2.5
high (310 K)	652	25

of 1 μg of sulfate for a system containing 5 μg of $(NH_4)_2SO_4$ versus a system containing 50 μg of $(NH_4)_2SO_4$ will result in an increase in NH_3^F by 0.35 μg for both cases. The additional NH_3^F will react with the available HNO_3^T producing the same amount of NH_4NO_3 for each case. Thus, [d(PM)/d(sulfate)] shown in Figure 2 is independent of the initial sulfate concentration.

For GR < 0.5, [d(PM)/d(sulfate)] is approximately constant, −0.28. Adding sulfate to the system when GR < 0.5 decreases the total PM. Although this behavior seems counterintuitive, its explanation is based on the resulting behavior of NH_4NO_3. In this regime (low GR), there is excess nitrate, and most of the ammonia is in the aerosol phase. Adding 1 μmol of sulfate requires 2 μmol of ammonia for neutralization. As most of the ammonia is in the form of NH_4NO_3, 2 μmol of NH_4NO_3 will be removed so that the additional sulfate will be neutralized by the now available NH_3. Two micromoles of NH_4NO_3 is approximately 160 μg, and 1 μmol of $(NH_4)_2SO_4$ is approximately 132 μg, and hence, removing 2 μmol of ammonium nitrate and adding 1 μmol of ammonium sulfate results in a net loss of total mass. Although the PM response to sulfate is approximately constant in this region, its response is different than that expected. Previously, it was assumed [d(PM)/d(sulfate)] = 1.34, but in this region, [d(PM)/d(sulfate)] = −0.28. It should be noted that this behavior is expected at low NH_3^F, high HNO_3^T, and for low temperature.

For high GR, the predicted [d(PM)/d(sulfate)] ≈ 1.34, the same as if there were no ammonium nitrate present. In this case, there is excess ammonia in the system as all HNO_3^T is already in the form of NH_4NO_3. Adding sulfate to the system moves some of the excess ammonia from the gas phase, into the aerosol phase thus increasing the total PM; the con-

centration of NH_4NO_3 remains approximately constant. Hence, at high GR, [d(PM)/d(sulfate)] is constant, indicating an approximately linear response of PM with respect to sulfate, the same as previously assumed. For GR between 0.5 and 1.5, [d(PM)/d(sulfate)] increases from −0.28 to 1.34 indicating a nonlinear response of PM with respect to total sulfate.

From our analysis, a critical GR for sulfate, R_{cs}, can be defined as the upper boundary for nonlinear regimes such that if

$$GR < R_{cs} \qquad (3)$$

the PM level will respond nonlinearly with respect to total sulfate. For example, for $[HNO_3^T] > 5$ ppb, $R_{cs} \approx 1.1$ as seen in Figure 2.

Regions where [d(PM)/d(sulfate)] is discontinuous or does not correspond to observed ambient conditions are not shown in Figure 2. For example, for $HNO_3^T = 1$ ppb, [d(PM)/d(sulfate)] is not shown for GR < 0.13 nor for GR > 40, which correspond to NH_3^F concentrations of less than 0.13 and greater than 40 ppb, respectively. When GR < 0.13 for $HNO_3^T = 1$ ppb, the corresponding NH_3^F concentration is low and NH_4NO_3 formation is not possible as eq 1 is not satisfied. In this case, the PM response to sulfate is linear, [d(PM)/d(sulfate)] = 1.34, since NH_4NO_3 is not present. Hence, to the left of the given curves, the PM reponse to sulfate is as previously assumed. The maximum NH_3^F concentration considered in this study is 40 ppb, and therefore, [d(PM)/d(sulfate)] is examined up to GR = 40 for $HNO_3^T = 1$ ppb. Figure 2 is applicable for all NH_3^F concentrations less than 40 ppb and for nonzero NH_4NO_3.

A similar analysis can be performed for a range of atmospheric conditions. For example, at moderate temperatures and low rh, K is high (45 ppb^2) and the formation of NH_4NO_3 will not be as favorable as for low temperatures or high rh. For GR < 1, [d(PM)/d(sulfate)] ranges from approximately −0.2 to 0.5 when NH_4NO_3 is present. In this GR range, [d(PM)/d(sulfate)] is negative as GR approaches zero for high HNO_3^T (>15 ppb). The reason for this behavior is similar to that given for low-temperature conditions. For low HNO_3^T (<10 ppb) at GR < 1, [d(PM)/d(sulfate)] remains positive as little NH_4NO_3 is present. An increase in PM will
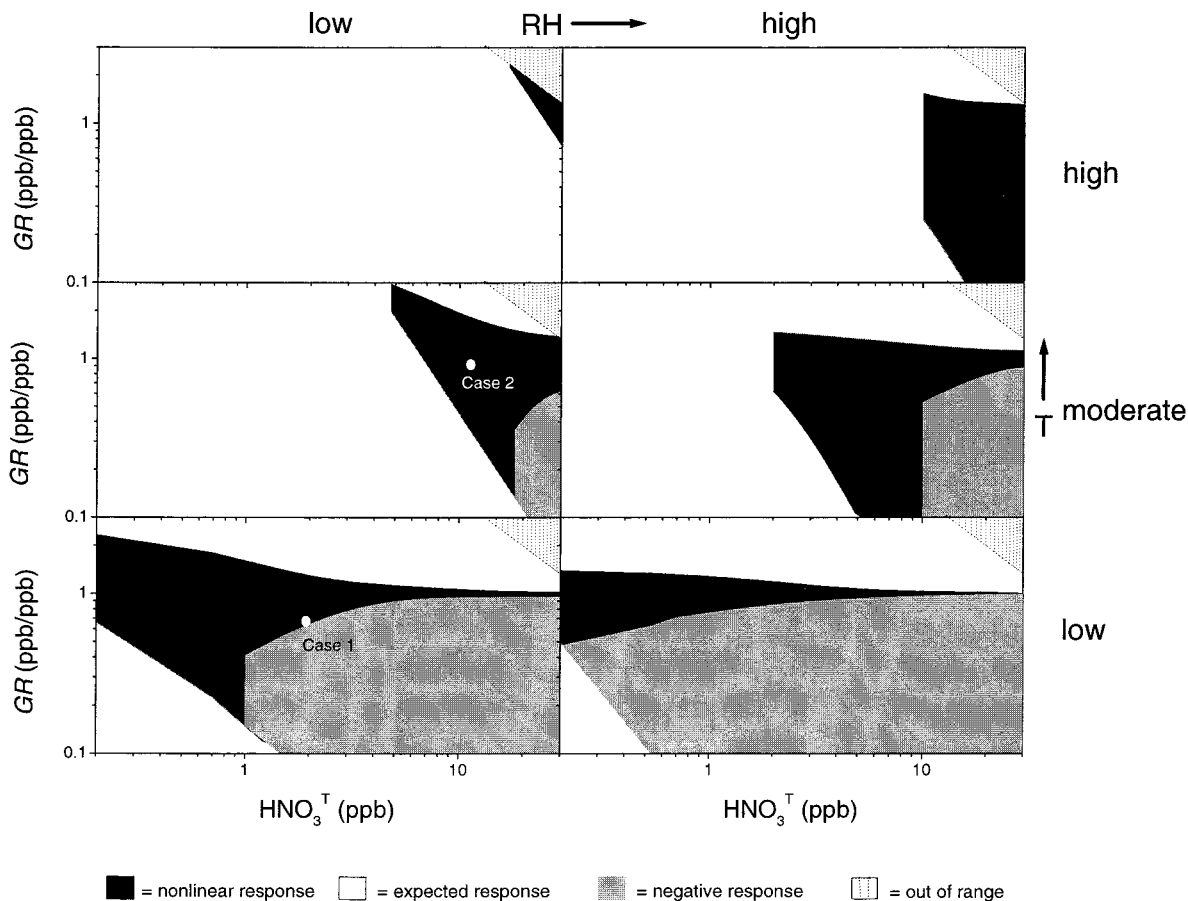
FIGURE 3. Regions of PM response to sulfate for low (30%) and high (90%) rh and low (275 K), moderate (298 K), and high (310 K) temperatures. For negative, nonlinear, and expected responses, [d(PM)/d(sulfate)] = − 0.28−0, 0−1, and 1−1.34, respectively.

occur with the addition of sulfate as NH_3 is taken from the gas into the aerosol phase. In the intermediate GR range (1−2), nitrate and sulfate are competing for available ammonia producing nonlinear behavior. Over the high GR range, there is excess ammonia in the system, and it readily neutralizes any additional sulfate while the NH_4NO_3 concentration remains approximately constant. R_{cs} can be determined given [d(PM)/d(sulfate)] as a function of GR. For example, $R_{cs} = 2.9$ for $HNO_3^T = 5$ ppb.

To facilitate the determination of the PM response to sulfate for a given system, a single expression can be developed indicating possible regions of nonlinearity. Equations 1 and 3 represent upper and lower bounds for nonlinear regions of [d(PM)/d(sulfate)] and, thus, can be combined into a single expression. Dividing both sides of eq 1 by $[HNO_3^T]^2$

$$\frac{K}{[HNO_3^T]^2} < GR \qquad (4)$$

and combining eqs 3 with 4

$$\frac{K}{[HNO_3^T]^2} < GR < R_{cs} \qquad (5)$$

which defines the region for a possible nonlinear response of PM with respect to sulfate. Given the total ammonia, nitric acid, and sulfate concentrations of a system, GR can be calculated, and with appropriate values for K and R_{cs} determined above, it can be determined if eq 5 is satisfied.

Figure 3 shows the resultant regions calculated with eq 5 for a range of temperatures (low = 275 K, moderate = 298 K, high = 310 K) and low (30%) and high (90%) rh. In the

case for [d(PM)/d(sulfate)], "expected response" refers to cases where [d(PM)/d(sulfate)] = 1−1.34, "nonlinear response" to cases where [d(PM)/d(sulfate)] = 0−1, and "negative response" to cases where [d(PM)/d(sulfate)] < 0. The expected response region is smallest for conditions of low temperature which favor the formation of NH_4NO_3. The expected response region increases as the temperature increases where the formation of NH_4NO_3 becomes less favorable. At high temperatures, $(NH_4)_2SO_4$ dominates the aerosol phase as little NH_4NO_3 is present and a reduction in sulfate will result in an equivalent loss of $(NH_4)_2SO_4$. No NH_4NO_3 will form from the available ammonia and thus, [d(PM)/d(sulfate)] = 1.34. At low temperatures, however, NH_4NO_3 will likely form from any ammonia made available from a reduction in sulfate; [d(PM)/d(sulfate)] = − 0.28−1.0 and nonlinear and negative responses dominate.

PM Response to Ammonia

As the PM level may respond linearly or nonlinearly with respect to ammonia, [d(PM)/d(ammonia)] is analyzed to determine boundaries for these regions. Figure 4 shows [d(PM)/d(ammonia)] as a function of GR for moderate temperatures and high rh at fixed HNO_3^T and variable sulfate concentrations. At low GR (<1), the PM level responds nonlinearly to changes in ammonia concentrations, [d(PM)/d(ammonia)] is greater than 2.5. In such regions, the system is characterized by low NH_3^F and HNO_3^T. For the given conditions (high rh), which favor NH_4NO_3 formation, any additional ammonia will readily bind with the available nitric acid to form NH_4NO_3. High GRs (>3) are characterized by high ammonia concentrations where most of the HNO_3^T present is already in the form of NH_4NO_3. There is little gaseous nitric acid present at high GR, and adding ammonia
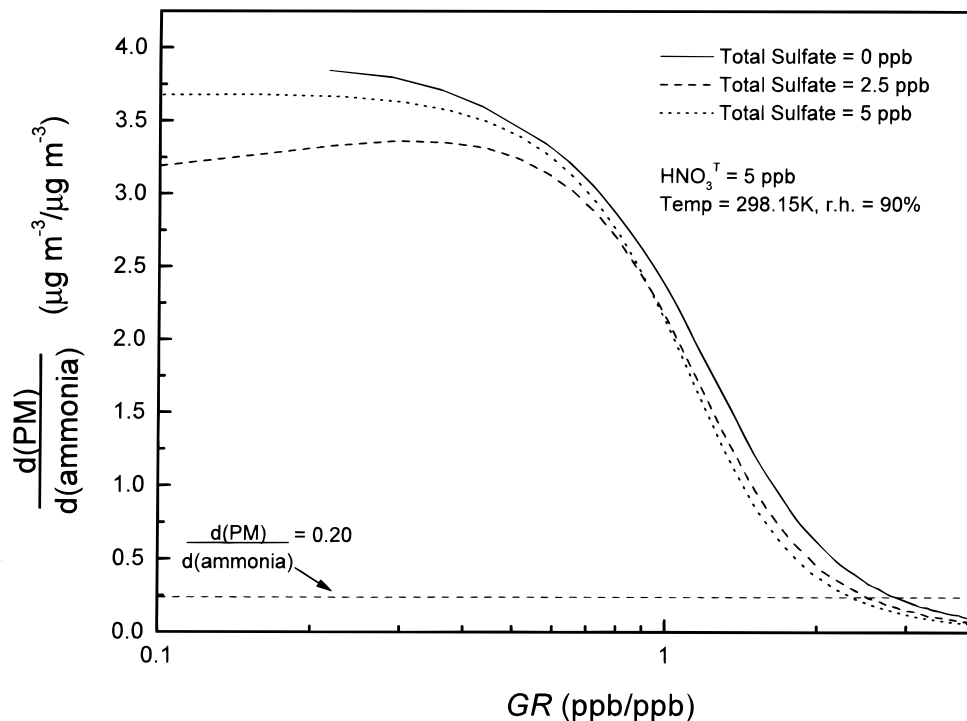
FIGURE 4. [d(PM)/d(ammonia)] as a function of GR for a range of sulfate concentrations and fixed HNO_3^T at moderate (298 K) temperatures and high (90%) rh.

does not significantly affect the PM level. For our purposes, we define regions where [d(PM)/d(ammonia)] < 0.2 as cases where the PM level is not sensitive to ammonia availability. For GR from 1 to 3, [d(PM)/d(ammonia)] varies from 2.5 to approximately 0, indicating a nonlinear response of PM with respect to ammonia. Adding more ammonia eventually causes lower [d(PM)/d(ammonia)] values as nitric acid becomes scarce and less NH_4NO_3 is formed decreasing the total PM.

Figure 4 also shows that [d(PM)/d(ammonia)] is greater at low sulfate concentrations than for high concentrations. K is high at high ionic strength fractions corresponding to low sulfate concentrations (*14*). Because of the high K, there is more nitric acid available for formation of NH_4NO_3 when ammonia is added to the system. As a result, more NH_4NO_3 is formed. When the aerosol is dry, K, and thus [d(PM)/d(ammonia)], is independent of sulfate concentration. With the zero sulfate line as a worst case scenario, the PM level will respond nonlinearly with respect to ammonia for GR less than 2.9. Therefore, the zero sulfate line ensures that nonlinear regions are not mistaken for cases where the PM concentration is insensitive to changes in ammonia. For the purposes of our study, it is safer to assume the PM level will respond nonlinearly rather than as previously assumed. Thus, for the following [d(PM)/d(ammonia)] estimations, the sulfate concentration will be set to zero.

Critical gas ratios for ammonia (R_{ca}) can be defined as done for the PM response to sulfate with eq 3. For conditions of low temperature and rh, R_{ca} is 1.3, 1.2, and 1.1, respectively, for nitrate levels of 5, 10, and 15 ppb. Below R_{ca}, [d(PM)/d(ammonia)] is significant; the PM level responds nonlinearly to ammonia. High nitrate concentrations result in low R_{ca} decreasing the nonlinear region. At such concentrations, much of the nitrate present is already in the aerosol phase. Any additional ammonia has little nitric acid to react with to form NH_4NO_3, thus, having little effect on the PM level. An additional linear region, however, is also noted in Figure 4 for low GR (<0.5) and high nitric acid concentrations (>10 ppb) at moderate temperatures and high rh; [d(PM)/

d(ammonia)] $\approx$ 3.5 in this case. For such low temperatures, K is small ($\sim$0.1 ppb^2) allowing the formation of NH_4NO_3 from even small amounts of ammonia and nitric acid. At low GR, there is excess nitric acid and any additional ammonia will be converted to NH_4NO_3. Regions where [d(PM)/d(ammonia)] for a given nitrate level is unrealistic or is discontinuous occur when maximum concentrations are reached (to the right of the curve) or where NH_4NO_3 formation is not possible as eq 1 is not satisfied (to the left of the curve).

For moderate temperatures and low rh R_{ca} is 7.0, 4.0, and 3.0, respectively, for nitrate levels of 5, 10, and 15 ppb, which are higher than for R_{ca} for low temperatures and high rh. A linear region at low GR (<1) is not observed as moderate temperatures do not favor the formation of NH_4NO_3. Similar analyses can be conducted over a range of atmospheric conditions and regions of PM response to ammonia can be determined with an equation similar to eq 5. Figure 5 shows the results for a range of temperatures and for low and high rh. Regions defined as "no response" are for cases where the PM level is not sensitive to ammonia, [d(PM)/d(ammonia)] < 0.2. For regions noted as "very sensitive response", [d(PM)/d(ammonia)] = 3.5–4.7, and for "nonlinear response", [d(PM)/d(ammonia)] = 0.2–3.5. No response regions are largest for conditions where little to no NH_4NO_3 is present.

Similarities between the response of PM to sulfate and ammonia can be determined from Figures 3 and 5. Previous assumptions concerning PM behavior to sulfate (expected response region) and to ammonia (no response region) are valid for high temperature and low rh as little NH_4NO_3 is present. However, nonlinear response regions extend to low GR ($\sim$1–2) for the PM response to sulfate and high GR ($\sim$10) for the response to ammonia. For the PM response to ammonia, a large excess of NH_3^F (high GR) is required before the system enters a "zero response" region. However, for the response to sulfate, such high NH_3^F is not necessary for the system to enter an expected response region. In addition, the nonlinear response region for the PM response to ammonia is defined where [d(PM)/d(ammonia)] varies from
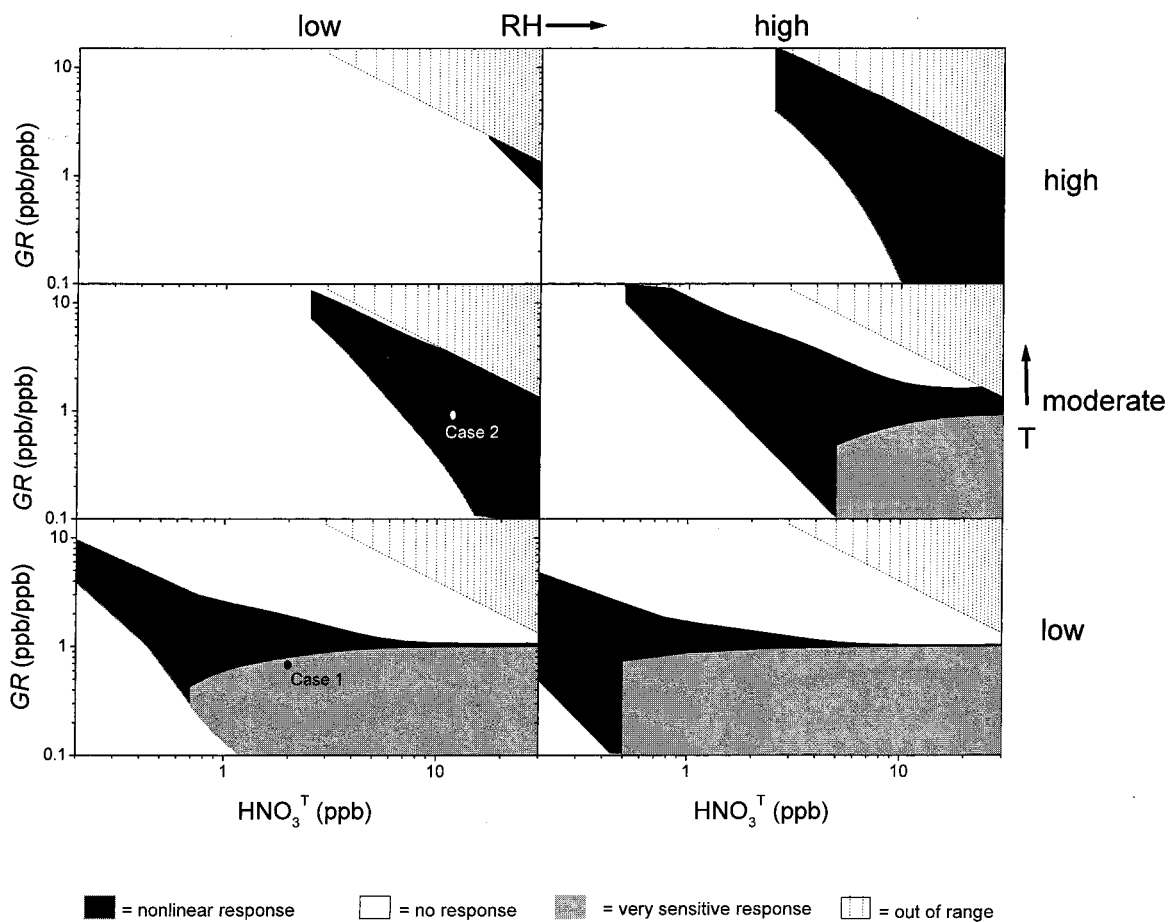
FIGURE 5. Regions of PM response to ammonia for low (30%) and high (90%) rh and low (275 K), moderate (298 K), and high (310 K) temperatures. For zero, nonlinear and very sensitive responses, [d(PM)/d(ammonia)] = 0−0.2, 0.2−3.5, and 3.5−4.7, respectively.

0.2 to 3.5 whereas to sulfate, the nonlinear response region is defined where [d(PM)/d(sulfate)] varies from 0 to 1.00. Thus, the nonlinear regions of PM response to ammonia are larger as these regions generally cover a broader range of GR as compared to those for the response to sulfate.

PM Response to Nitrate

The role of nitric acid in the behavior of total PM is expected to be similar to that of ammonia. Figure 6 shows [d(PM)/d(nitrate)] for fixed free ammonia and variable sulfate concentrations at moderate temperatures and high rh. For low sulfate concentrations, [d(PM)/d(nitrate)] as a function of GR is variable (nonlinear PM response to nitrate) throughout the GR range. An approximately linear region is present for GR > 3 for high sulfate concentrations, but as GR increases, [d(PM)/d(nitrate)] starts decreasing. The rate of decrease at high GR increases with decreasing sulfate concentration, and thus, the sulfate concentration has a significant effect on the behavior of PM with respect to nitric acid at high GR and high rh. In light of this dependence, an average sulfate concentration of 1 ppb will be used in all high rh simulations of PM response to nitrate. Significantly lower sulfate concentrations will result in nonlinear PM behavior at all NH_3^F and HNO_3^T. For higher concentrations of sulfate, a sulfate concentration of 1 ppb can be thought of as a "worst case" scenario. For these cases, a sulfate concentration of 1 ppb ensures that nonlinear regions are not mistaken for regions where the PM concentration responds linearly to nitrate. A total sulfate concentration of 1 ppb will be used for all PM response to nitrate simulations. Again, at low rh, the aerosol is dry and the PM behavior is independent of sulfate concentration.

As seen in Figure 6, two linear regions are present, where [d(PM)/d(nitrate)] approaches 0 and 0.9. The following ranges of [d(PM)/d(nitrate)] will be used to define regions of PM response to nitrate: 0.0−0.1 (expected response), 0.1−0.9 (nonlinear response), and 0.9−1.3 (positive response). For GR < 1, the expected response is present for conditions of moderate temperature and low rh; there is an excess amount of nitrate and adding more nitric acid does little to the total PM concentration. At high GR, there is excess ammonia in the system, and addition of nitric acid produces NH_4NO_3. In the intermediate GR range, the transition between the two linear regions occurs as [d(PM)/d(nitrate)] ranges from 0.1−0.90. At different temperatures and rh, the behavior of PM to nitrate is similar to that given for [d(PM)/d(ammonia)].

In constructing diagrams of PM response to nitrate, a single equation such as eq 5 and 6 cannot be used to define nonlinear or expected response regions where a critical GR (R_{cn}) can be used. As NH_3^F is the independent variable in this case, eq 5 needs to be determined as a function of NH_3^F instead of HNO_3^T. Hence, multiplying eq 1 by [NH_3^F]

$$GR < \frac{[NH_3^F]^2}{K} \qquad (6)$$

which defines the upper bound for GR. A lower bound for GR can be established by the definition of GR:

$$GR > \frac{[NH_3^F]}{30} \qquad (7)$$
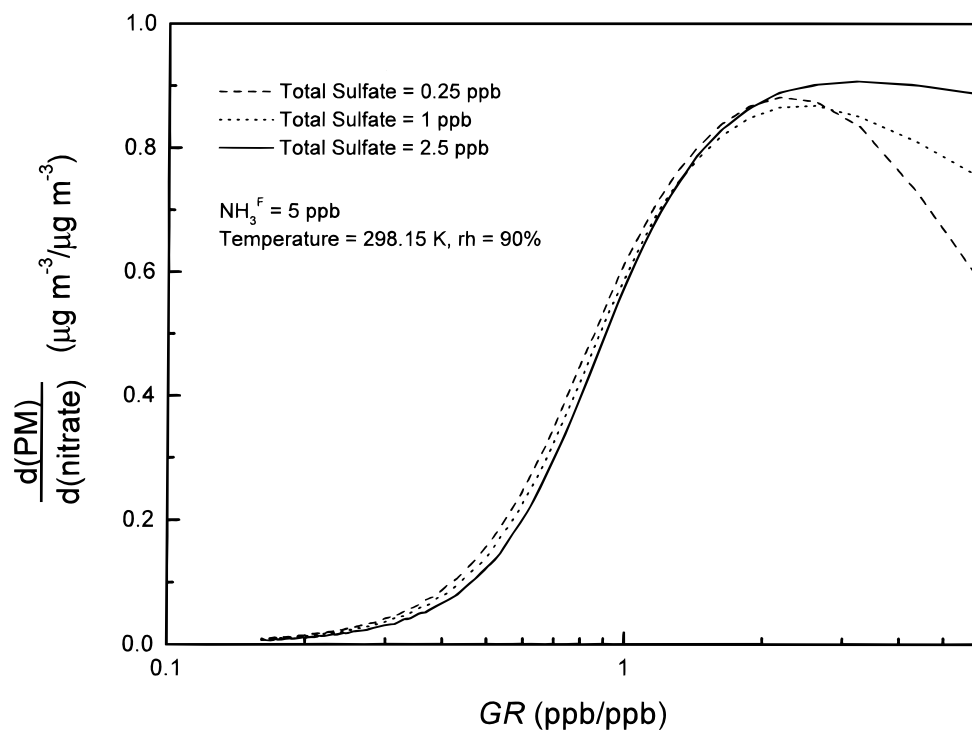
where 30 ppb is the maximum HNO_3^T concentration.

FIGURE 6. [d(PM)/d(nitrate)] as a function of GR for a range of sulfate concentrations and fixed NH_3^F at moderate temperatures (298 K) and high rh (90%).

Combining eqs 6 and 7:

$$\frac{[NH_3^F]^2}{K} > GR > \frac{[NH_3^F]}{30} \qquad (8)$$

Figure 7 shows the resulting regions over a range of temperatures and for low and high rh from eq 8. Areas noted as positive response correspond to cases where [d(PM)/d(nitrate)] > 0.9, expected response to [d(PM)/d(nitrate)] = 0−0.1 and nonlinear response to [d(PM)/d(nitrate)] = 0.1−0.9. As for the PM response to sulfate and ammonia, expected response regions correspond to conditions opposing the formation of NH_4NO_3. With little to no NH_4NO_3, a small change in HNO_3^T will have no effect on the overall PM concentration level.

Application to Individual Locations

The results presented can be applied to directly estimate the PM response to reductions in precursor concentrations. For example, how would the PM level respond to 20% reductions each in sulfate, total ammonia, and total nitric acid in a given region? Will the PM level respond linearly when sulfate is reduced? Two examples are presented below.

Table 2 lists the total ammonia, nitrate, and sulfate concentrations and atmospheric conditions for two representative urban polluted areas. These choices of concentrations and atmospheric conditions were motivated by average measured levels reported for Warren, MI (15), and Los Angeles, CA (4). Case 1 is characterized by a GR of 0.67 and wintertime conditions (low temperature, low rh). With these conditions and based on the diagrams in Figures 3, 5, and 7, case 1 is in nonlinear response regions of PM with respect to sulfate and nitrate, and a very sensitive response region with respect to ammonia. Thus, the PM level for case 1 should behave nontrivially to changes in sulfate, nitrate, and ammonia. Table 3 shows the simulated behavior of the PM for case 1 as a function of 20% reductions in the precursor concentrations using GFEMN. A reduction in each of the

precursor concentrations results in net reductions in PM concentrations. Reducing sulfate decreases the total $(NH_4)_2SO_4$ concentration, but increases NH_4NO_3. In this case, [d(PM)/d(sulfate)] = 0.19. Reductions in nitrate and ammonia have no effect on the $(NH_4)_2SO_4$ concentration, but reduce NH_4NO_3, thus decreasing the PM concentration. As ammonia is reduced, HNO_3 is made available from the reduction in NH_4NO_3; $HNO_3(g)$ thus increases. Similarly, a nitrate reduction resulting in the reduction of NH_4NO_3 frees up ammonia which moves into the gas phase; $NH_3(g)$ increases. The reduction in ammonia has the most significant impact on the reduction of total PM while sulfate and nitrate have similar effects on PM. Hence, for each precursor reduction, the PM response does not match previous assumptions. The simulations of the PM behavior agree with the direct estimations from the diagrams in Figures 3, 5, and 7.

Furthermore, the diagrams showing the behavior of PM can be used to determine when the PM behavior will move from a particular response region into another. For example, case 1 is initially characterized by GR = 0.67 which corresponds to a nonlinear response of PM to sulfate. As a precursor concentration is changed, GR changes as well. For example, if NH_3^T were reduced by 50%, the resulting GR would be 0.34. In this case, case 1 is now in a negative response region for the PM response to sulfate. Thus, the diagrams in Figures 3, 5, and 7 can also be used to directly estimate how the PM response moves from one regime into another. The possibility of moving into different PM response regions should be taken into consideration in applying the diagrams in Figures 3, 5, and 7 as GR changes with precursor concentrations.

Case 2 is characterized by high levels of particulate concentrations and a GR of 0.91. With the appropriate diagrams in Figures 3, 5, and 7, the PM level is predicted to respond nonlinearly with respect to sulfate, nitrate, and ammonia. Table 3 shows the directly estimated PM response to 20% reductions in each of the precursor concentrations for case 2. The behavior of the individual gas and aerosol phase components is similar to that for case 1. For the PM
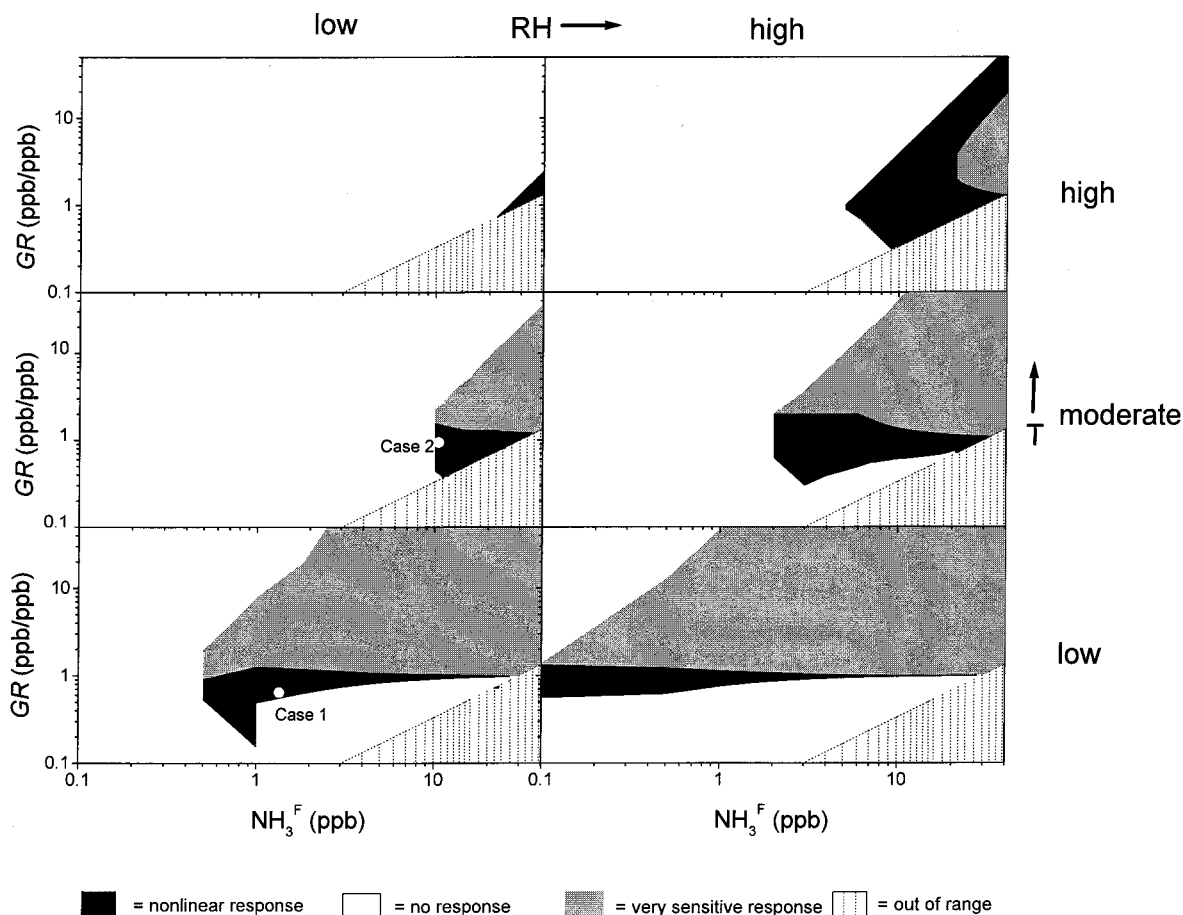
FIGURE 7. Regions of PM response to nitrate for low (30%) and high (90%) rh and low (275 K), moderate (298 K), and high (310 K) temperatures. For expected, nonlinear, and positive responses, [d(PM)/d(nitrate)] = 0−0.1, 0.1−0.9, 0.9−1.27, respectively.

TABLE 2. Atmospheric Conditions and Concentrations for Two Urban Polluted Areas

case	region type	conditions	HNO_3^T ($\mu g\ m^{-3}$)	NH_3^T ($\mu g\ m^{-3}$)	sulfate ($\mu g\ m^{-3}$)	HNO_3^T (ppb)	NH_3^F (ppb)	GR
1	urban, low pollution	wintertime	5.56	3.00	5.63	2.00	1.34	0.67
2	urban, high pollution	summertime	29.28	10.52	9.41	11.40	10.32	0.91

TABLE 3. Gas- and Aerosol-Phase Concentrations for 20% Reductions in Precursor Concentrations for Cases 1 and 2[a]

		precursor reduction	NH_3(g)	HNO_3(g)	NH_4NO_3	$(NH_4)_2SO_4$	PM	ΔPM	Δ(PM)/ Δ(precursor)
case 1	initial		0.13	2.16	4.32	7.59	11.90		
	Δ(sulfate)	1.12	0.24	1.14	5.62	6.07	11.69	0.21	0.19
	Δ(nitrate)	1.11	0.20	1.34	3.95	7.59	11.54	0.37	0.33
	Δ(ammonia)	0.60	0.07	4.16	1.78	7.59	9.37	2.53	4.22
case 2	initial		4.32	18.43	13.78	12.68	26.46		
	Δ(sulfate)	1.88	4.64	17.18	15.37	10.14	25.52	0.74	0.39
	Δ(nitrate)	5.86	5.12	15.54	10.01	12.68	22.69	3.57	0.61
	Δ(ammonia)	2.1	3.46	23.02	7.95	12.68	20.63	5.63	2.68

[a] All concentrations are in micrograms per cubic meter.

response to sulfate, [d(PM)/d(sulfate)] = 0.5 and the decrease in sulfate is partially offset by an increase in NH_4NO_3. In addition, [Δ(PM)/Δ(ammonia)] and [Δ(PM)/Δ(nitrate)] are 2.68 and 0.61, respectively. A 20% reduction in ammonia has a greater impact on the PM response as ammonia has a lower molecular weight resulting in a greater molar reduction compared to nitrate. Hence, case 2 is another example where the PM will respond nontrivially to precursor concentration reductions based on the diagrams of Figures 3, 5, and 7.

Discussion

Wolff (8) has noted that, in many instances, a fraction of the aerosol nitrate exists in the coarse mode. Coarse mode nitrate results mainly from reactions of HNO_3 with NaCl or dust (8, 9). As this study is based on $PM_{2.5}$ or accumulation mode aerosols, the diagrams in Figures 3, 5, and 7 can still be used despite the existence of coarse mode nitrate aerosols. Provided the coarse mode nitrate concentration is known or can be estimated, HNO_3^T can be adjusted by subtracting the

coarse mode nitrate concentration, thus allowing the use of the diagrams in determining PM behavior.

In determining the regions of PM response to precursor concentrations, it was assumed that changes in such concentrations occur independently of one another. However, this may not always hold true. Sulfate is formed heterogeneously in fogs and cloud droplets via the dissolution of gaseous SO_2, where the reactions of SO_2 leading to the formation of sulfate are pH dependent. Given the sensitivity of the cloud pH to the concentrations of ammonia and nitric acid, a change in the concentrations of these gases may thus introduce a change in the sulfate concentration. If it is desired to determine the PM response to ammonia where its reduction also introduces a change in the total sulfate concentration, for example, Figures 3, 5, and 7 can be used in a two-step manner provided the subsequent change in sulfate is known a priori or can be calculated independently. Figure 5 can be used to determine the PM response to ammonia, and then based on the resulting response, Figure 3 can be used to determine the PM response given the subsequent change in sulfate concentration.

In cases where the equilibrium time scale is long relative to the residence time of particles in a given environment, thermodynamic equilibrium may not be a good approximation in predicting aerosol behavior (16, 17). Wexler and Seinfeld (16) developed an expression for the equilibrium time scale which suggests that aerosol populations with large aerosol sizes will have equilibrium time scales on the order of hours. However, for small aerosol sizes, the time scale is on the order of seconds, and equilibrium is expected to be a valid assumption. As this study is concerned mainly with $PM_{2.5}$, thermodynamic equilibrium is probably an adequate approximation in predicting average PM behavior.

Hence, regimes of PM response to precursor concentrations (sulfuric acid, ammonia, and nitric acid) have been defined by use of the equilibrium model, GFEMN. On the basis of the relationships developed between inorganic PM and its major inorganic components, the PM level response with respect to ammonia, sulfate, and nitric acid given the total precursor concentrations and ambient conditions can be easily estimated. Expected PM responses to precursor reductions are most evident for high temperature and low rh as these conditions prevent the formation of NH_4NO_3. Under such conditions, the PM level responds linearly to sulfate and is insensitive to ammonia and nitrate. Some interesting regions noted include regions where the PM level actually increases with decreasing sulfate concentration (low GR, low temperature) and where the PM level responds to ammonia with $[d(PM)/d(ammonia)]$ as high as 4.7. Ap-plications to two different areas showed that PM responses to example precursor concentrations behave nontrivially and not necessarily as previously assumed. Previous assumptions concerning the PM response to precursor concentrations hold only under specific atmospheric conditions and precursor concentrations. For the two examples, reductions in ammonia emissions have the most significant impact on the total PM level, although such a reduction would substantially increase the atmospheric acidity. The diagrams in Figures 3, 5, and 7 can also be used to show how the PM response moves from one response region into another as precursor concentrations change.

Literature Cited

(1) Tanner, R. L.; Marlow W. H.; Newman L. *Environ. Sci. Technol.* **1979**, *13*, 75−78.
(2) Saxena, P.; Hudischewskyj, A. B.; Seigneur, C.; Seinfeld, J. H. *Atmos. Environ.* **1986**, *20*, 1471−1483.
(3) Watson, J. G.; Chow, J. C.; Lurmann, F.; Musarra, S. *J. Air Waste Manage. Assoc.* **1994**, *44*, 405−412.
(4) Chow, J. C.; Watson, J. G.; Lowenthal, D. H.; Solomon, P. A.; Magliano, K. L.; Ziman, S. D.; Richards L. W. *Aerosol Sci. Technol.* **1993**, *19*, 105−128.
(5) Chow J. C.; Watson J. G.; Fujita E. M.; Lu L.; Lawson D. R.; Ashbaugh L. L. *Atmos. Environ.* **1994**, *28*, 2061−2080.
(6) AIRS, Aerometric Information Retrieval System (database). PM_{10} and $PM_{2.5}$ data; U. S. Environmental Protection Agency, Office of Air Quality Planning and Standards: Research Triangle Park, NC, 1995.
(7) U. S. Environmental Agency, **1996**; Vol. 1, Report no. EPA/600/ P-95/001aF.
(8) Wolff, G. T. *Atmos. Environ.* **1984**, *18*, 977−981.
(9) Richards, L. W. *Atmos. Environ.* **1983**, *17*, 397−402.
(10) Ansari, A. S.; Pandis, S. N. *Atmos. Environ.* In press.
(11) Pierson, W. R.; Brachczek, W. W.; Gorse, R. A.; Japar, S. M.; Norbeck, J. M.; Keeler, G. J. *Atmos. Environ.* **1989**, *23*, 431−459.
(12) Stevens R. K.; Dzubay T. G.; Russwurm G.; Rickel D. *Atmos. Environ.* **1978**, *12*, 55−68.
(13) Stelson A. W.; Seinfeld, J. H. *Atmos. Environ.* **1982**, *16*, 983−982.
(14) Stelson A. W.; Seinfeld J. H. *Atmos. Environ.* **1982**, *16*, 2507−2514.
(15) Cadle, S. H. *Atmos. Environ.* **1985**, *19*, 181−188.
(16) Wexler, A. S.; Seinfeld, J. H. *Atmos. Environ.* **1990**, *24A*, 1231−1246.
(17) Meng, Z.; Seinfeld, J. H. *Atmos. Environ.* **1996**, *30*, 2889−2900.