8.   AMMONIUM NITRATE EQUILIBRIUM

This section evaluates the extent to which the Northern Front Range is ammonia-rich (or anion-deficient) with regard to the formation of secondary ammonium nitrate and ammonium sulfate. Changes in ammonia or nitric acid precursor concentrations do not necessarily affect ammonium nitrate concentrations in the same way. Ammonia concentrations might increase with emissions (e.g., larger fertilizer applications, a larger number of farm animals) or from reductions in sulfur dioxide emissions that would provide less sulfuric acid to react with existing ammonia. Conversely, ammonia emissions reductions owing to urbanization might reduce ammonia concentrations. The Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE) method represents the atmospheric equilibrium between gas and particle phases for the ammonium nitrate/nitric acid/ammonia system. SCAPE is applied to measurements from the Brighton and Welby sites to estimate the consequences of potential changes in nitric acid, ammonia, and ammonium sulfate concentrations on ammonium nitrate levels.

8.1   Ammonium Nitrate Equilibrium and Interaction with Sulfate

Ammonium nitrate, ammonium sulfate, ammonium bisulfate, and sulfuric acid result from gaseous emissions of sulfur dioxide, nitrogen oxides, and ammonia. Since precursor gases are not always emitted by the same sources and undergo complicated chemical reactions in the atmosphere, it is not always the case that reductions in their emissions will result in proportional reductions in the ambient concentrations of their particulate end-products.

Sulfur dioxide gas converts to particulate sulfate through gas- and aqueous-phase transformation pathways. In the gas-phase pathway, sunlight induces photochemical reactions that create oxidizing species (hydroxyl radicals) that react with a wide variety of atmospheric constituents in a way that adds oxygen atoms to their chemical structures. Transformation rates range from less than 0.01%/hr to about 5%/hr (Calvert and Stockwell, 1983). The transformation rate appears to be controlled more by the presence or absence of the hydroxyl radical and its competing reactions with other gases than by the sulfur dioxide concentration.

In the presence of fogs or clouds, sulfur dioxide dissolves in droplets where it experiences aqueous reactions that are much faster than gas-phase reactions. The major aqueous phase pathways for the oxidation of sulfur dioxide to sulfate involve dissolved ozone or hydrogen peroxide. Other pathways include oxidation by dissolved oxygen in the presence of trace metals and oxidation by nitrates. When ammonia is also dissolved in the droplet, the sulfuric acid is neutralized to ammonium sulfate. As relative humidity decreases below 100% (i.e., the fog or cloud evaporates), the sulfate particle is present as a small droplet that includes a portion of liquid water. As the relative humidity further decreases, the droplet evaporates and a small, solid sulfate particle remains.

The relative humidity at which this occurs depends on the composition of the drop and other factors. Liquid water has been associated in the laboratory with pure ammonium sulfate drops at relative humidities as low as 30% (Tang, 1980), far below the deliquescence

relative humidity of 80%. Similar phenomena have been associated with natural aerosols (Rood et. al., 1989). The reactions within the fog droplet are very fast, and the rate is controlled by the solubility of the precursor gases. Aqueous transformation rates of dissolved sulfur dioxide to sulfate are 10 to 100 times faster than gas-phase rates.

Nitric oxide converts to nitrogen dioxide, primarily by reaction with ozone. Nitrogen dioxide can: 1) change back to nitric oxide in the presence of ultraviolet radiation; 2) change to short-lived species that participate in other chemical reactions; 3) form organic nitrates; or 4) oxidize to nitric acid. The major pathway to nitric acid is reaction with the same hydroxyl radicals that transform sulfur dioxide to sulfuric acid. Nitric acid deposits from the atmosphere fairly rapidly; however, in the presence of ammonia it is neutralized to particulate ammonium nitrate. Conversion rates for nitrogen dioxide to nitric acid range from less than 1%/hr to 90%/hr; they are typically five to ten times the conversion rates for sulfate formation. Though they vary throughout a 24-hour period, these rates are significant during both daytime and nighttime hours, in contrast to the gas-phase sulfate chemistry that is most active during the day.

While ammonium sulfate is a fairly stable compound, ammonium nitrate is not. Its equilibrium with gaseous ammonia and nitric acid is strongly influenced by temperature and relative humidity. The gas phase is highly favored when ambient temperatures approach or exceed 35 °C, while the particulate ammonium nitrate phase is highly favored when temperatures are less than 15 °C. When gaseous ammonia or nitric acid concentrations are reduced, some of the particulate ammonium nitrate evaporates to regain equilibrium with the gas phase. Ammonium nitrate particles on a filter may disappear during sampling or between sampling and analysis with changes in temperature and gas concentrations. The ammonium nitrate contribution to $PM_{2.5}$ is underestimated in many studies because special sampling procedures are needed to accurately quantify concentrations of this atmospheric constituent. Such procedures were applied in NFRAQS (Chow et al., 1998) to obtain accurate particle nitrate concentrations.

Sulfur dioxide to particulate sulfate and nitrogen oxides to particulate nitrate reactions compete with each other for available hydroxyl radicals and ammonia. Ammonia reacts preferentially with sulfuric acid to form ammonium bisulfate and ammonium sulfate, and the amount of ammonium nitrate formed is only significant when the total ammonia exceeds the sulfate by a factor of two or more on a mole basis. Chow et al. (1998) show that sulfate measured during NFRAQS is completely neutralized and in the form of ammonium sulfate. Reducing sulfur dioxide emissions might result in ammonium nitrate increases that exceed the reductions in ammonium sulfate where there is a dearth of ammonia.

The Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE) method (Kim et al., 1993a, 1993b; Kim and Seinfeld, 1995) apportions sodium, nitrate, sulfate, ammonium, and chloride among gas, liquid, and solid phases using thermodynamic equilibrium theory. For the NFRAQS application, SCAPE reactions couple the nitrate/ammonia/sulfate chemical system. The ammonia that is not scavenged by sulfate is referred to as "free ammonia." The most important SCAPE component for the Northern Front Range is the combination of nitric acid and ammonia that forms ammonium nitrate. The equilibrium constant for this reaction is both relative humidity (RH) and temperature dependent (Stelson

and Seinfeld, 1982). Ammonium nitrate formation is favored under conditions of high relative humidity and low temperature, and these conditions were common during the NFRAQS Winter 97 intensive operating period.

SCAPE was applied to measurements of three-hour nitrate, ammonium, and gaseous nitric acid and ammonia from the Sequential Gas Sampler (SGS) at the Welby and Brighton sites. Sulfate, sodium, chlorine, and water-soluble potassium concentrations were estimated from the collocated six-and twelve-hour samples taken with the sequential filter sampler (SFS), assuming that these longer averages were uniform over the three-hour periods that they comprised. Hourly surface temperature and relative humidity measurements at these sites were averaged over the three-hour sampling intervals to correspond to the air quality measurements.

Fujita et al. (1998) evaluated the SCAPE simulations and the ambient data to which they were applied. Several discrepancies were found in the three-hour data sets, and SCAPE was applied to 101 samples that were determined be of sufficient quality for evaluating the effects of changes in precursors on ammonium nitrate levels. The remaining samples showed evidence of insufficient quality for SCAPE simulations owing to lack of simultaneous measurements, large temperature and humidity deviations within the averaging periods, and inconsistencies between the three-hour SGS and six-hour SFS measurements. Fujita et al. (1998) also compared simulated and measured particle and gaseous species and evaluate their sensitivity to temperature and relative humidity changes within the three-hour sampling periods. These comparisons were within the ranges expected from reported measurement uncertainties and environmental variations over the sample duration.

8.2 Effects of Ammonia, Nitric Acid, and Sulfate Changes

As shown in Section 6, ammonia concentrations are high along the Northern Front Range, especially in the down-valley, non-urban areas. A measure of the amount of ammonia available relative to the amount of nitrate and sulfate is the molar ratio of total ammonia to the sum of total nitrate and twice the amount of sulfate. A molar ratio exceeding unity means that there is sufficient ammonia available to neutralize all available nitrate and sulfate. Higher temperatures and lower relative humidities mitigate against this neutralization, however.

Figure 8.2-1 shows this molar ratio as a function of particle nitrate concentration for the three-hour measurements at Welby and Brighton. The molar ratio ranges from 1.2 to 34.8 with a mean value of 5.8. The molar ratio is typically lowest when particle nitrate concentrations are large. Figures 8.2-2 through 8.2-4 illustrate the effect of temperature and relative humidity on the fraction of nitrate in the particle phase. All calculations assume $1 \mu g/m^3$ of total sulfate and $4 \mu g/m^3$ of total nitrate, approximately equal to NFRAQS averages. For each figure, the six curves are obtained by setting the molar ion ratio discussed above to 0.5, 0.75, 1.0, 2.0, 5.0, and 10.0, respectively. These figures demonstrate how temperature increases result in lower particle nitrate fractions while relative humidity increases result in higher particle nitrate fractions. This occurs through temperature dependence of the solid/gas phase equilibrium constant and through the temperature dependence of relative humidity.

Changes in ammonium nitrate concentrations in response to changes in ammonia, nitric acid, and sulfate levels are examined in Figure 8.2-5 through 8.2-13. These represent the average of all 101 samples (Figures 8.2-5 through 8.2-7), a large nitrate concentration with a high molar ratio (Figures 8.2-8 through 8.2-10), and a moderate nitrate concentration with a low molar ratio (Figures 8.2-11 through 8.2-13). These situations illustrate the probable consequences of ammonia, nitric acid, and sulfate concentration changes for typical and extreme conditions encountered along the Northern Front Range.

The averages depicted in Figures 8.2-5 through 8.2-7 were derived from thousands of individual SCAPE simulations. A base-case ammonium nitrate value was estimated for each of the 101 valid samples using the three-hour average measurements for total ammonia (sum of particle and gas phases), nitrate (sum of particle and gas phases), six-hour sulfate, relative humidity, and temperature from the Welby and Brighton sites. Subsequent tests were compared to these base-case values. The ammonia, nitric acid, and sulfate concentrations were changed by factors of 0.1, 0.2, 0.3, 0.4, 0.5, 0.75, 1.0, 1.5, and 2.0 for each sample and the particulate ammonium nitrate was recalculated. These changes reflect the possible effects of emissions reductions on ambient concentrations. The "Ratio of Simulated Particle Nitrate to Base Case" on the vertical axis of each figure is the particle nitrate for each of these cases divided by the base-case particle nitrate, averaged for the 101 samples.

Figure 8.2-5 shows for the average situation that no increases in ammonium nitrate result from increases in ammonia concentrations. It also shows that a 25% reduction in ammonia results in a minor reduction in particle nitrate, and that a 50% ammonia reduction reduces particle nitrate by only 15%. After a 50% ammonia reduction, however, particulate nitrate decreases are nearly proportional to ammonia reductions. Ammonia levels must be reduced by more than half before large reductions of particulate nitrate are realized.

This contrasts with Figure 8.2-6 that shows how particulate nitrate would change, on average, with reductions in available nitric acid. The relationship is linear and proportional. Reductions in nitric acid, a consequence of reductions in oxides of nitrogen emissions, result in a direct and proportional reduction in $PM_{2.5}$ ammonium nitrate concentrations.
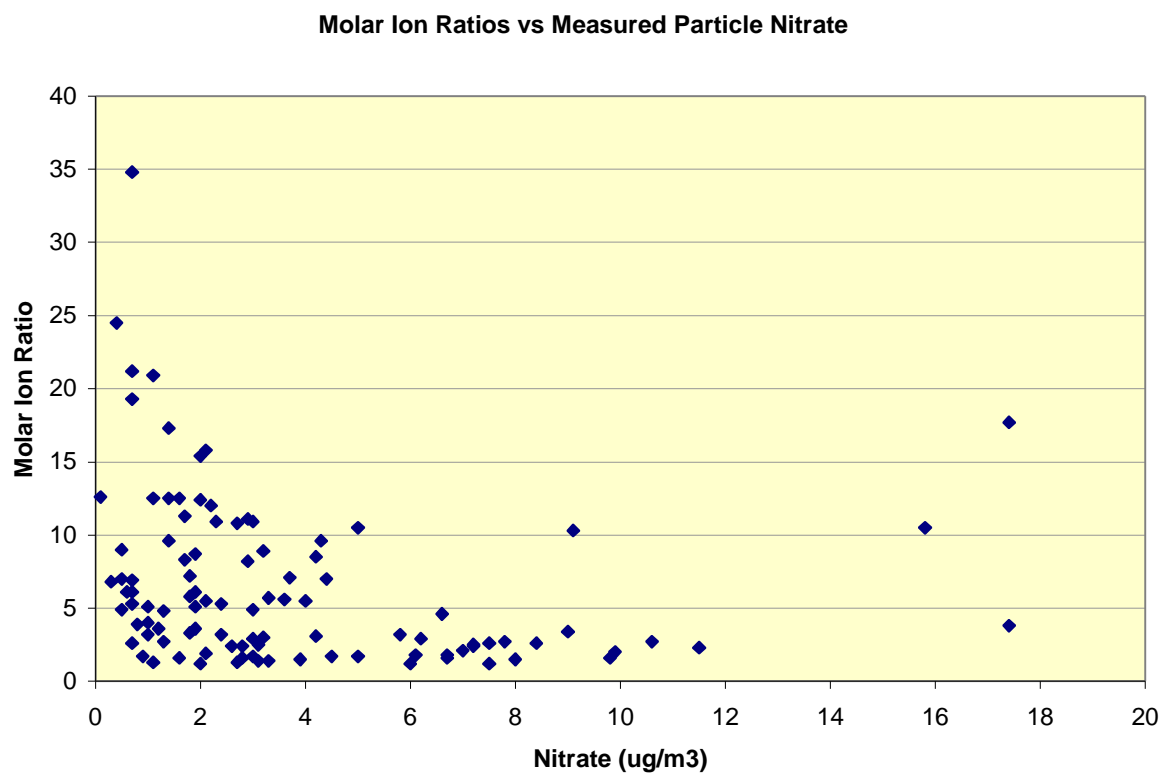
Figure 8.2-7 shows that there is no sensitivity to changes in sulfate levels. There is sufficient free ammonia along the Northern Front Range that the small amount freed by removing ammonium sulfate from the atmosphere has no effect on ammonium nitrate levels. There is a slight decrease in particulate nitrate with a doubling of ammonium sulfate, but sulfate concentrations would need to increase by more than double to engender even a slight decrease in ammonium nitrate concentrations.

The 01/19/97 1800 MST Brighton sample possessed a high molar ratio of 17.7 and a high nitrate concentration of 17.4 $\mu g/m^3$. As Figure 8.2-1 shows, this is the highest molar ratio for samples with more than 5 $\mu g/m^3$ of measured particle nitrate. Figures 8.2-8 through 8.2-10 express the same information as Figures 8.2-5 through 8.2-7 for this specific case to demonstrate what might occur for a very high molar ratio. Figure 8.2-8 shows no change in particle nitrate concentrations when ammonia changes, regardless of the amount of reduction down to 10% of the original concentration. There is so much ammonia available in this case that reductions of more than 90% would be needed before even a minor change in
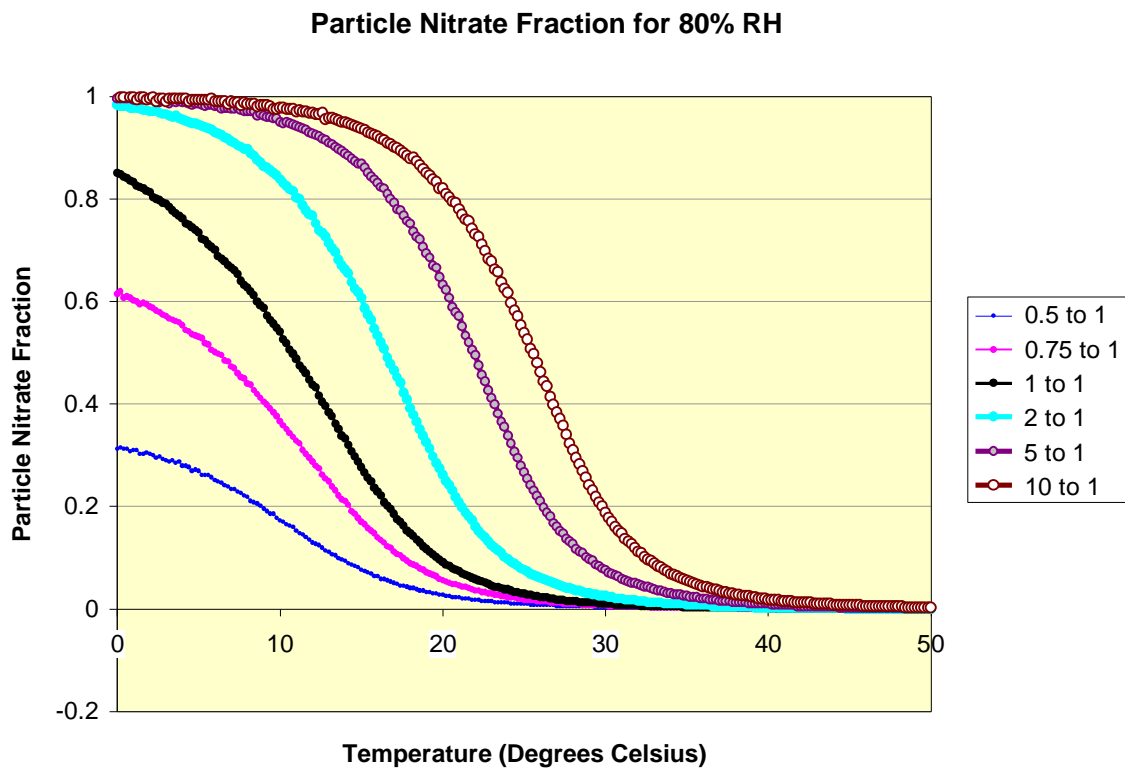
ammonium nitrate would occur. The responses to nitric acid and sulfate changes in this extreme case are similar to those of the average case. Only reductions in nitric acid, resulting from reductions in nitrogen oxides, will have any effect on $PM_{2.5}$ nitrate concentrations.

The 01/14/97 1200 MST Brighton sample possessed a low molar ratio of 1.2 and a moderate particle nitrate concentration of 7.5 $\mu g/m^3$. As Figure 8.2-1 shows, this is the lowest molar ratio for those cases involving more than 5 $\mu g/m^3$ of measured particle nitrate. Figures 8.2-11 through 8.2-13 show the results for this extreme. In contrast to the average and high molar ratio cases, particle nitrate decreases linearly and proportionally with reductions in ammonia. The same is true for nitric acid reductions. Particulate ammonium nitrate does not increase with twice the nitric acid or ammonia for this situation. As for the other cases, changes in sulfate concentrations have negligible effects on particulate nitrate levels.
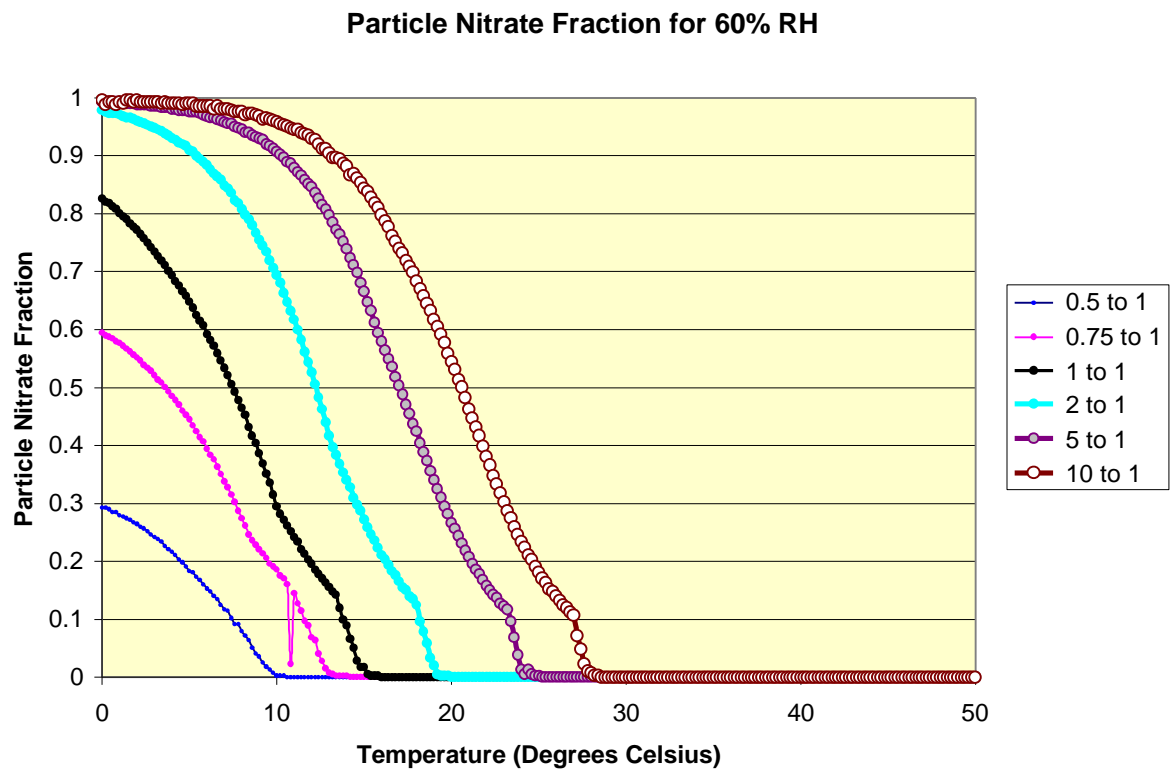
For most of the samples taken at the Welby and Brighton sites, particle ammonium nitrate was limited by the availability of nitric acid. Ammonium nitrate concentrations were not limiting. The Denver area, as represented by measurements at Welby and Brighton during wintertime periods with high $PM_{2.5}$ levels, is ammonia rich with regard to the formation of secondary ammonium nitrate and ammonium sulfate. On average, more than half of the ammonia needs to be removed before changes in $PM_{2.5}$ are obtained. Sometimes, however, either ammonia or nitric acid reductions will result in decreases in ammonium nitrate concentrations.

Molar Ion Ratios vs Measured Particle Nitrate

Figure 8.2-1. Molar ratio of total ammonia to total sulfate and nitrate as a function of measured particle nitrate at the Welby and Brighton sites.
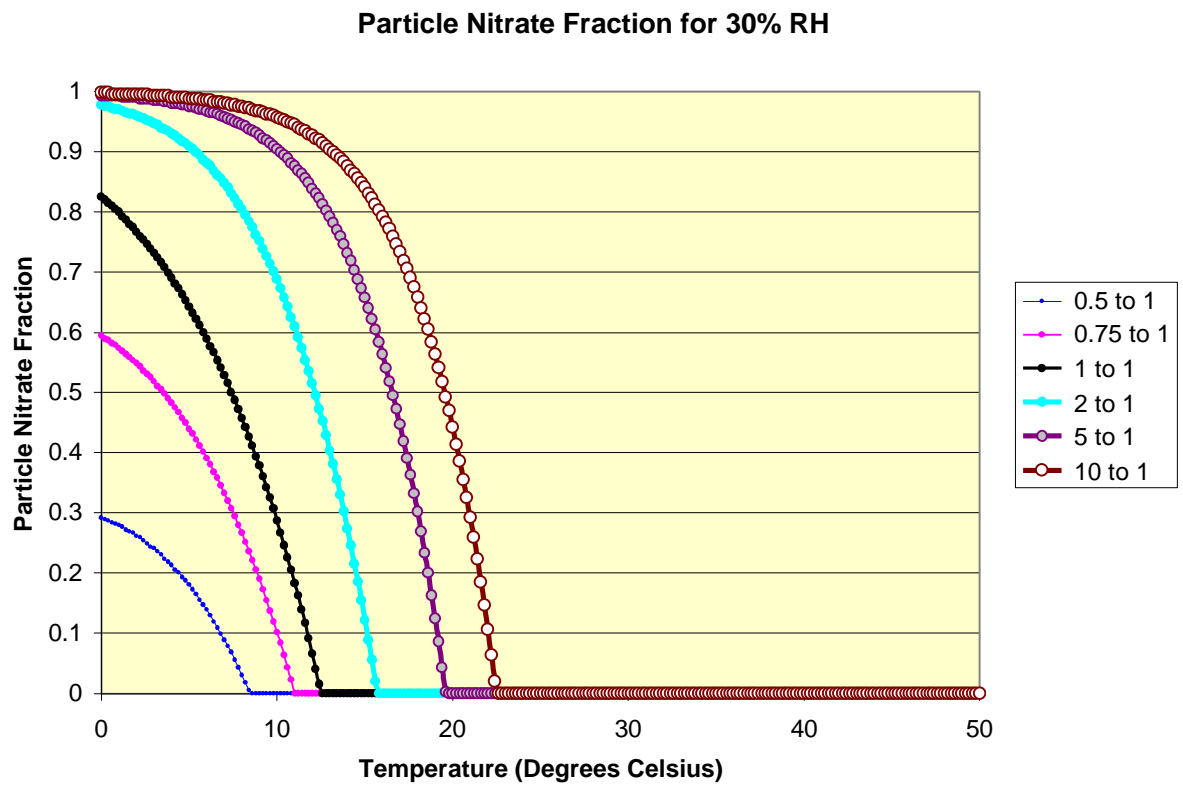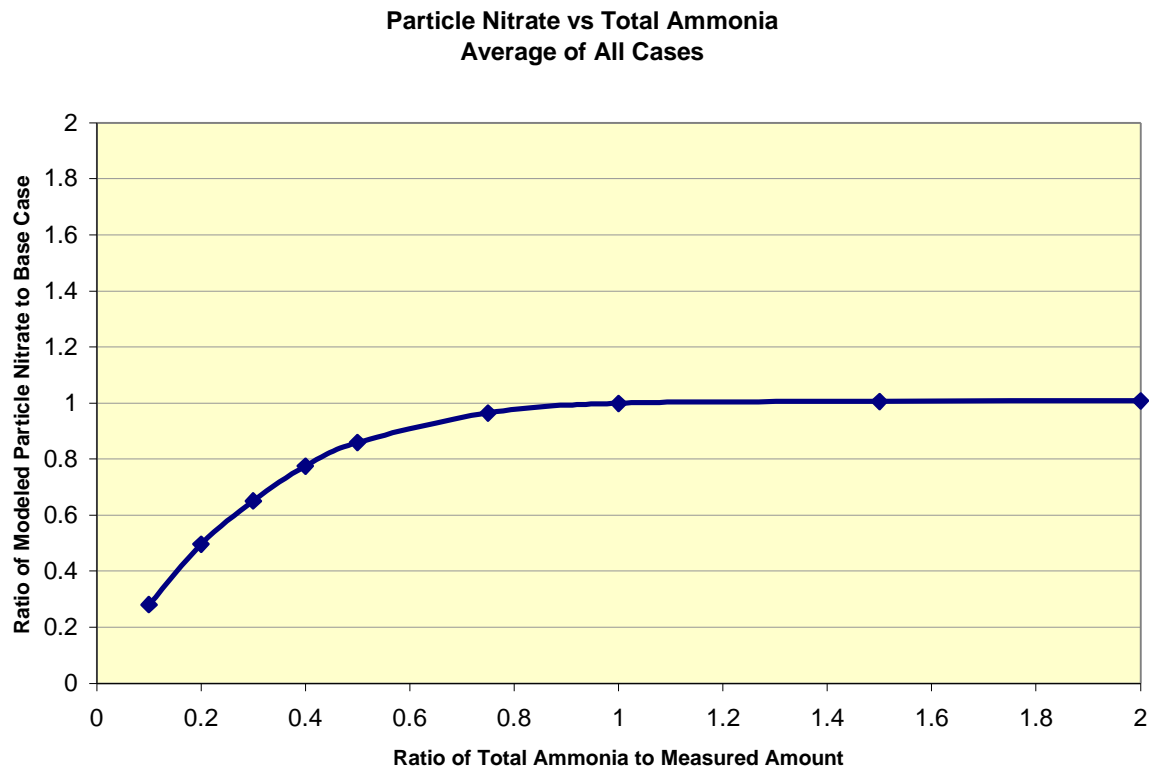
Particle Nitrate Fraction for 80% RH

Figure 8.2-2. Changes in particle nitrate in response to changes in temperature at 80% relative humidity.
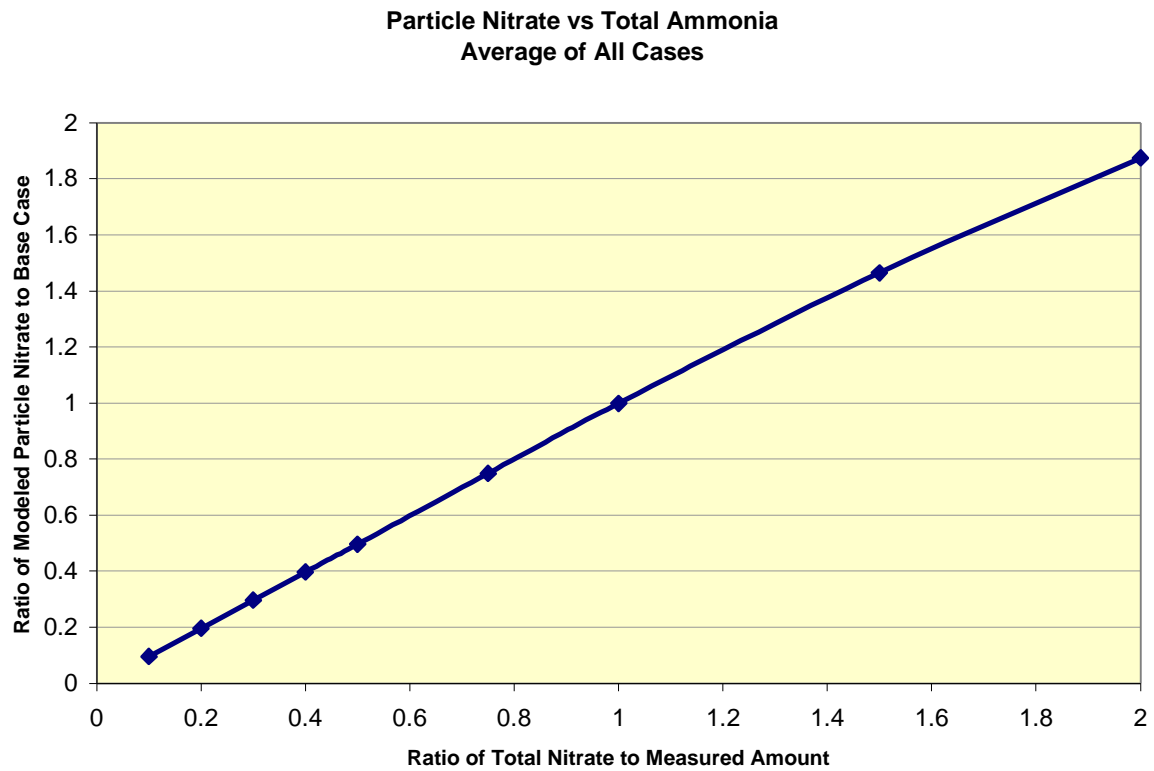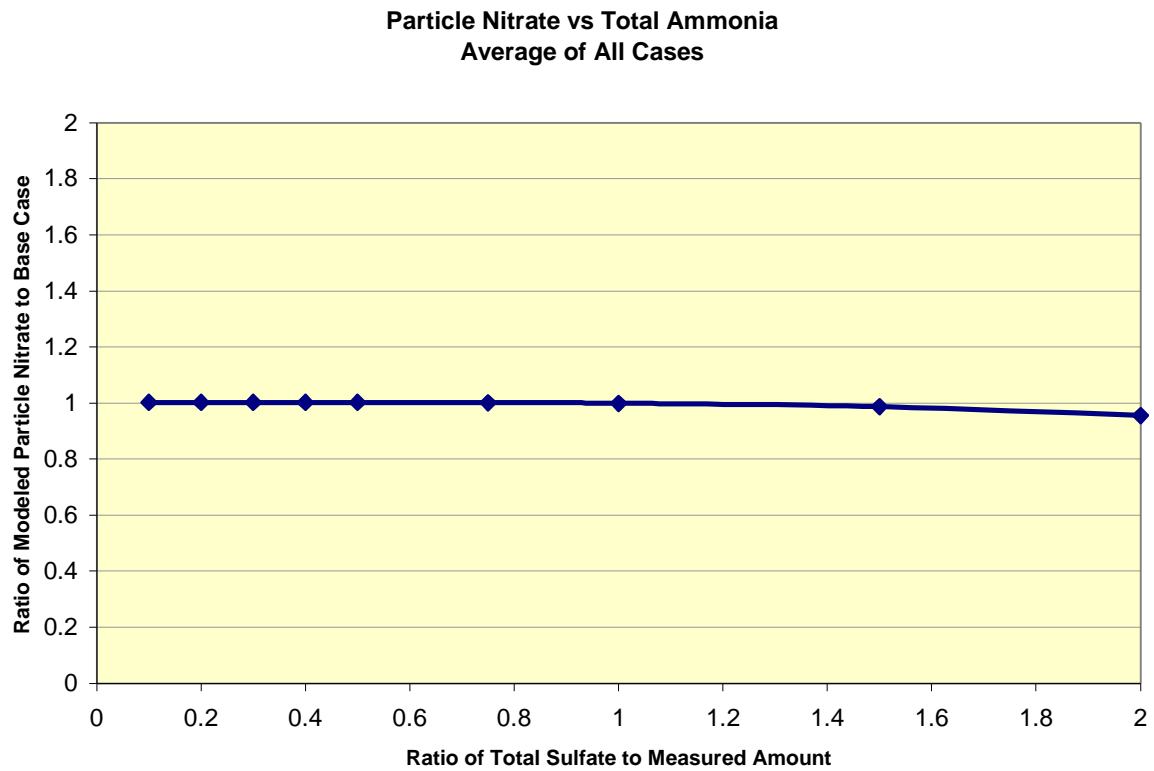
Particle Nitrate Fraction for 60% RH

Figure 8.2-3. Changes in particle nitrate in response to changes in temperature at 60% relative humidity.

Particle Nitrate Fraction for 30% RH

Figure 8.2-4. Changes in particle nitrate in response to changes in temperature at 30% relative humidity.

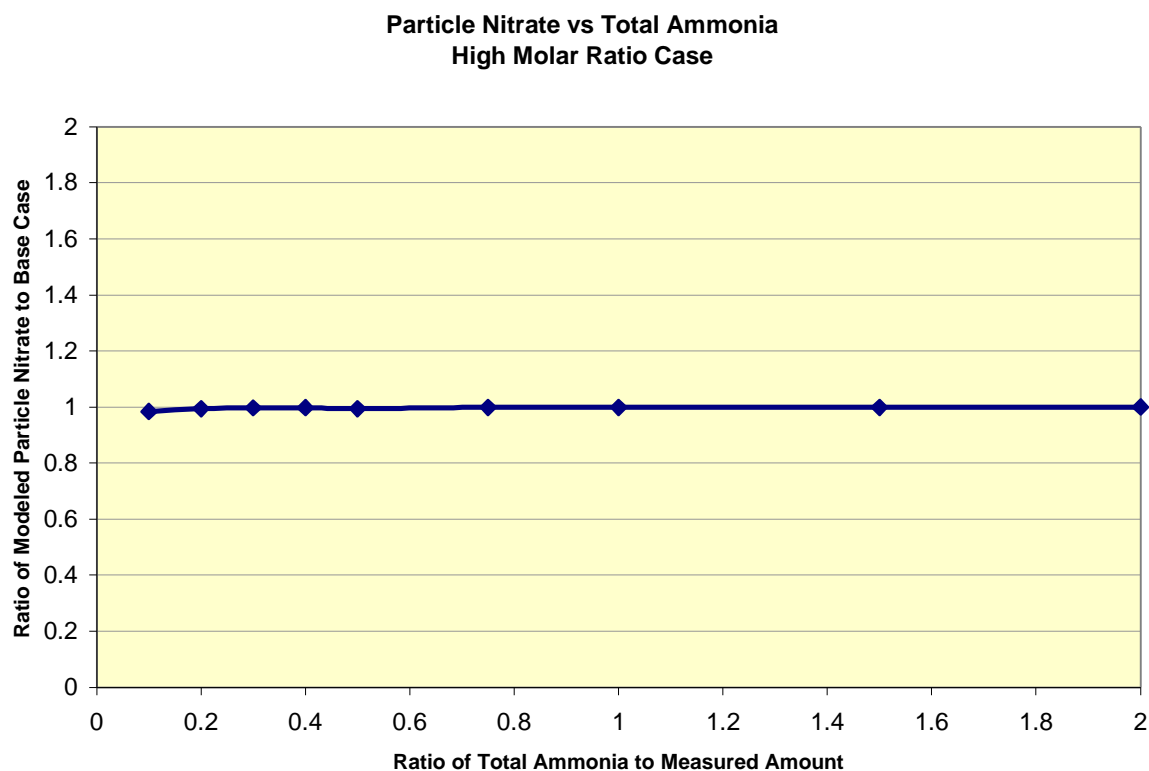**Particle Nitrate vs Total Ammonia**
Average of All Cases

Figure 8.2-5. Changes in particle nitrate concentrations in response to changes in ammonia. Results are averages for 101 separate three-hour samples at Welby and Brighton.

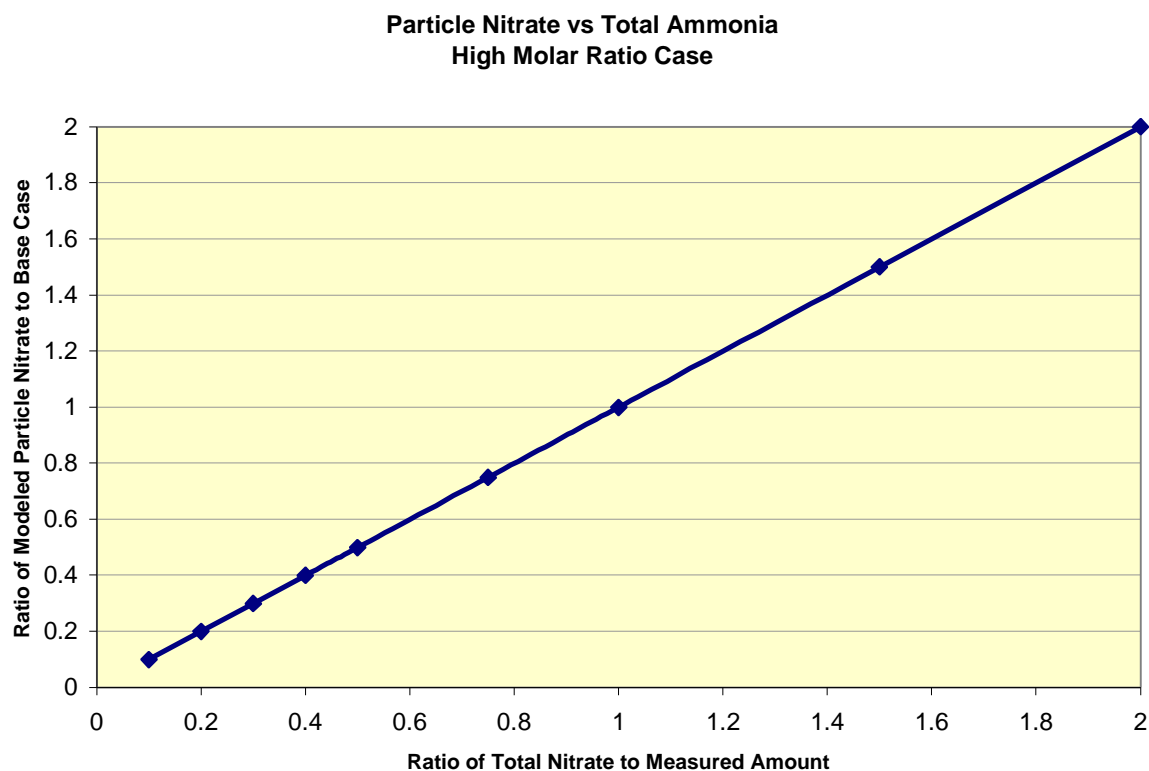**Particle Nitrate vs Total Ammonia**
Average of All Cases

Figure 8.2-6. Changes in particle nitrate concentrations in response to changes in nitric acid. Results are averages for 101 separate three-hour samples at Welby and Brighton.

Particle Nitrate vs Total Ammonia
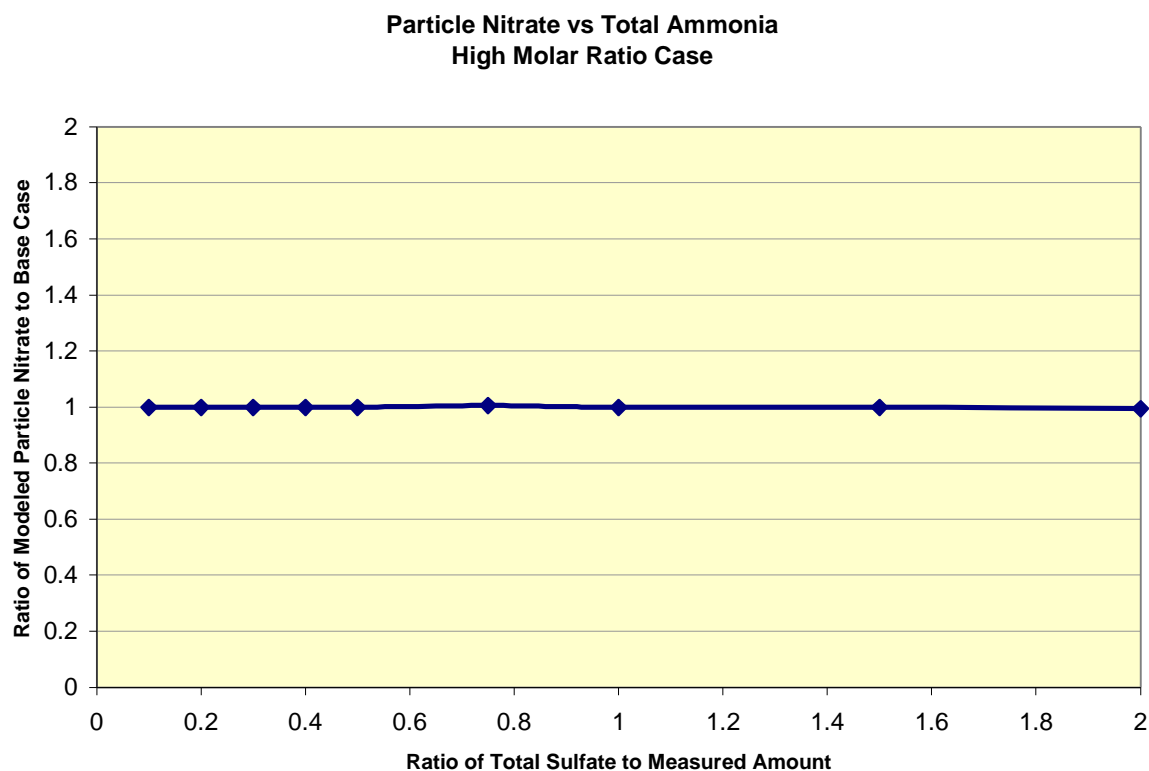**Average of All Cases**

Figure 8.2-7. Changes in particle nitrate concentrations in response to changes in sulfate. Results are averages for 101 separate three-hour samples at Welby and Brighton.

**Particle Nitrate vs Total Ammonia
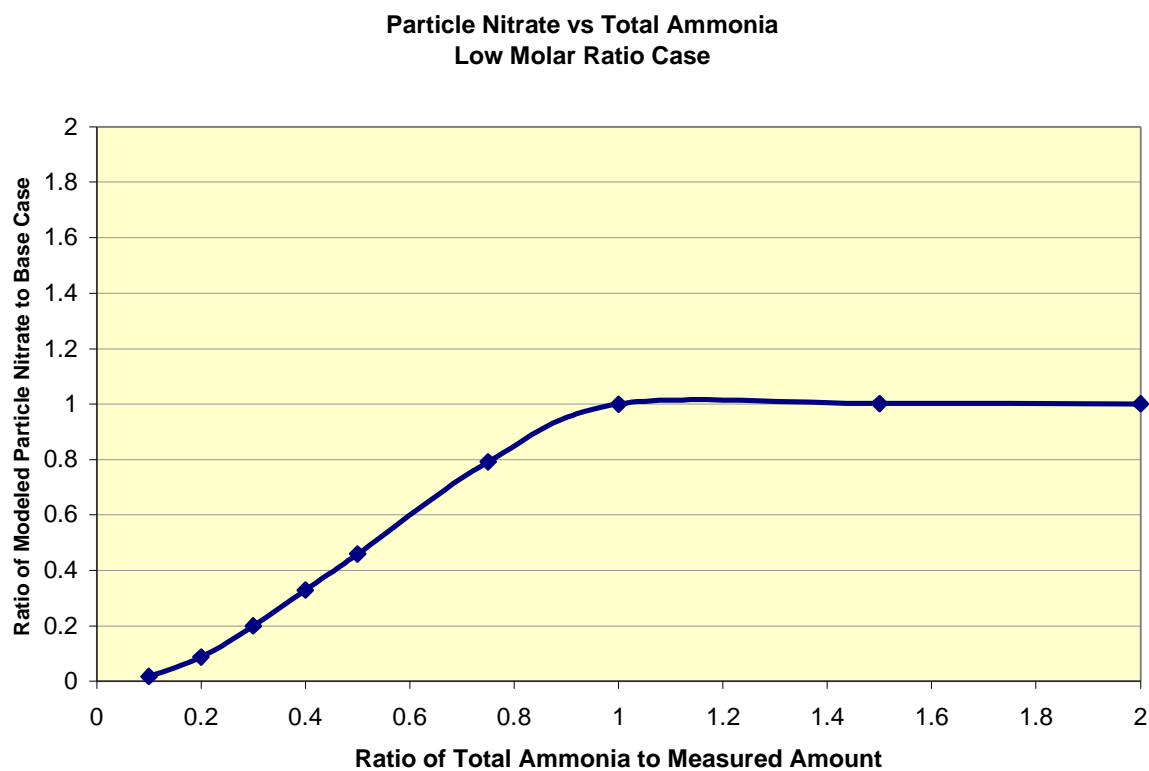High Molar Ratio Case**

Figure 8.2-8. Changes in particle nitrate concentrations in response to changes in ammonia. Results are for the 01/19/97 1800 MST Brighton sample.

**Particle Nitrate vs Total Ammonia
High Molar Ratio Case**

(y-axis: Ratio of Modeled Particle Nitrate to Base Case; x-axis: Ratio of Total Nitrate to Measured Amount)

Figure 8.2-9. Changes in particle nitrate concentrations in response to changes in nitric acid. Results are for the 01/19/97 1800 MST Brighton sample.

**Particle Nitrate vs Total Ammonia
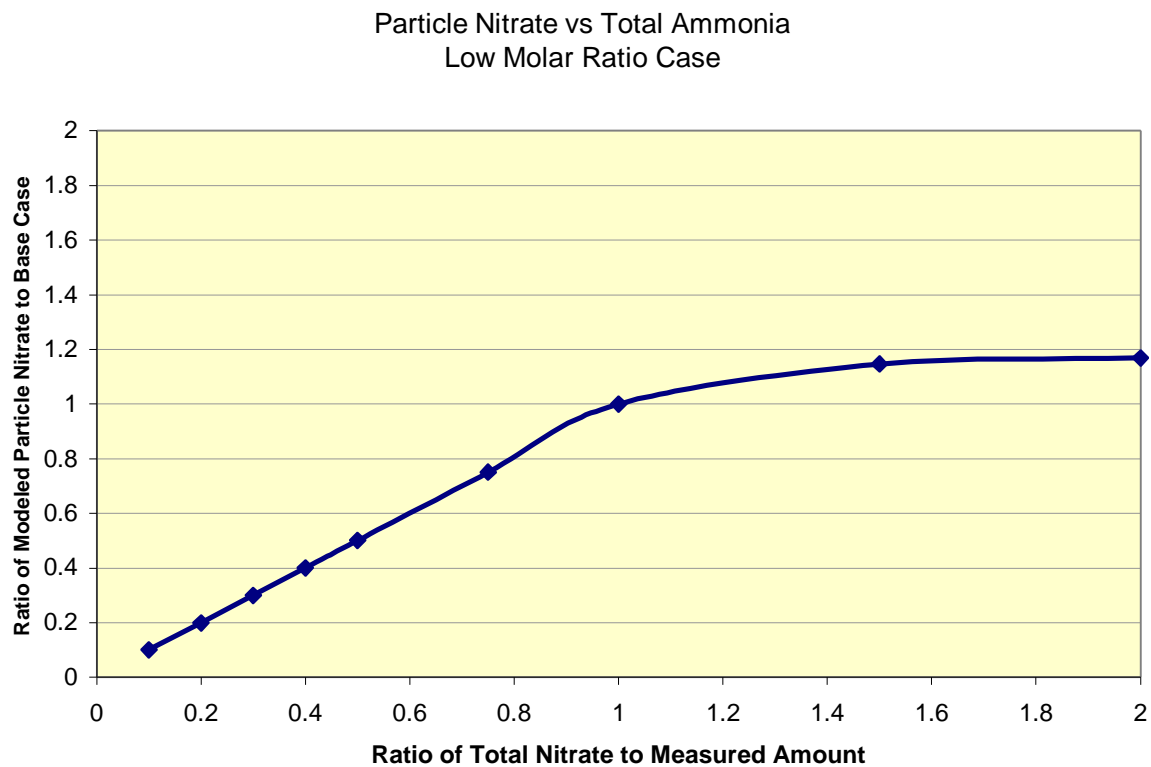High Molar Ratio Case**

Figure 8.2-10. Changes in particle nitrate concentrations in response to changes in sulfate. Results are for the 01/19/97 1800 MST Brighton sample.

Particle Nitrate vs Total Ammonia
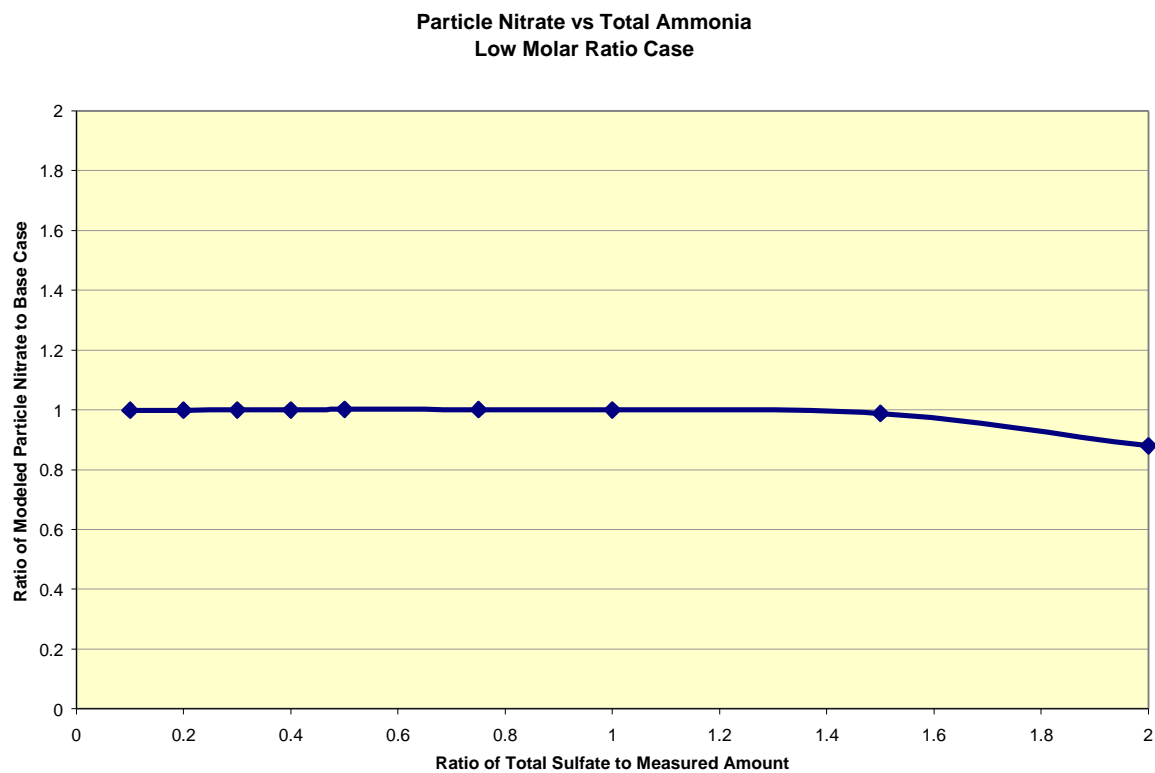**Low Molar Ratio Case**

Figure 8.2-11. Changes in particle nitrate concentrations in response to changes in ammonia. Results are for the 01/14/97 1200 MST Brighton sample.

Particle Nitrate vs Total Ammonia
Low Molar Ratio Case

Figure 8.2-12. Changes in particle nitrate concentrations in response to changes in nitric acid. Results are for the 01/14/97 1200 MST Brighton sample.

**Particle Nitrate vs Total Ammonia
Low Molar Ratio Case**

Figure 8.2-13. Changes in particle nitrate concentrations in response to changes in sulfate. Results are for the 01/14/97 1200 MST Brighton sample.