

AMMONIA AND NITRIC ACID CONCENTRATIONS
IN EQUILIBRIUM WITH ATMOSPHERIC AEROSOLS:
EXPERIMENT VS. THEORY

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ABSTRACT

The equilibrium between gaseous ammonia, nitric acid, and aerosol nitrate is discussed on the basis of a recent field experiment in Southern California. Comparison is drawn between theoretical equilibrium calculations and simultaneous measurements of nitric acid, ammonia, ammonium ion, nitrate ion, sulfate ion, other ionic species, temperature and dewpoint. Particulate and gaseous pollutant concentrations at some inland sampling sites are readily explained if the aerosol is assumed to exist as an external mixture with all particulate nitrate and ammonium available to form pure NH_4NO_3 . At other monitoring sites, especially near the coast, aerosol nitrate is found in the presence of NH_3 and HNO_3 concentrations that thermodynamic calculations show are too low to produce pure NH_4NO_3 . This can be explained when the amount of aerosol nitrate that can be derived from reaction of nitric acid with sea salt and soil dust is taken into account. A calculation approach that accounts for the presence of mixed sulfate and nitrate salts improves the agreement between predicted and observed pollutant concentrations in the majority of cases studied. Uncertainties in these calculations arise from a number of sources including the thermodynamic quantities, and the effect of these uncertainties on the comparison between theory and experiment is discussed.

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INTRODUCTION

Theoretical calculations for the formation of atmospheric aerosol nitrate based on thermodynamic equilibrium between ammonia, nitric acid and aerosol constituents have been presented recently by several research groups (Stelson et al., 1979; Stelson and Seinfeld, 1982 abc; Tang, 1976, 1980; Saxena and Peterson, 1981; Saxena et al., 1983; Bassett and Seinfeld, 1983). These chemical equilibrium calculations when embedded within a photochemical airshed model show promise of being able to predict the aerosol nitrate concentrations that will result from regional emissions of sulfurous, nitrogenous and hydrocarbon gaseous precursors (Russell et al., 1983).

Very few complete sets of atmospheric measurements exist, however, against which these chemical equilibrium calculations have been tested. Stelson et al. (1979) and Doyle et al. (1979) have shown that measurements of gaseous nitric acid and ammonia often are consistent with the upper limit on those concentrations predicted if the gases were in equilibrium with pure solid NH_4NO_3 . In those studies, the aerosol phase was not characterized completely, and little insight is gained into the cause of those cases where the atmospheric concentration products of NH_3 and HNO_3 fall below the equilibrium dissociation constant for pure NH_4NO_3 . The hypothesis that NH_3 , HNO_3 , and NH_4NO_3 are in equilibrium also has been pursued in cool humid atmospheres (Harrison and Pio, 1983) and at the low concentrations present in rural atmospheres (Cadle et al., 1982). Very little work has been published to date that examines the agreement between equilibrium-based calculation

schemes and field observations in cases where the ionic components in the aerosol are treated as being more complex than pure NH_4NO_3 . A step in this direction is provided by Tanner (1982), who compared the thermodynamics of aqueous mixed sulfate-nitrate solutions and solid ammonium nitrate to field experiments under conditions present on Long Island, New York.

In the present paper, the role of atmospheric nitric acid and ammonia in the formation of nitrate-containing aerosols is discussed on the basis of field experiments conducted in Southern California. Comparison is drawn between theoretical equilibrium calculations and an extensive collection of simultaneous observations on nitric acid, ammonia, ammonium ion, nitrate ion, sulfate ion, other ionic species, temperature and dewpoint. Calculations for the chemical equilibrium within multicomponent aerosols are contrasted to the results obtained if a pure NH_3 , HNO_3 , NH_4NO_3 system had been present. The case where non-volatile nitrates are present due to reaction between nitric acid and either sea salt or soil dust is considered. The effect of uncertainties in the thermochemical data required for these equilibrium calculations is discussed, as well as the implications that these uncertainties hold for verification studies of regional airshed models for aerosol nitrate formation.

EXPERIMENTAL

The measurements used in this comparison were taken on August 30-31, 1982, as part of a project designed to acquire an air quality model

validation data set for use in testing models for aerosol nitrate formation and transport. Gaseous nitric acid and ammonia, and aerosol sulfate, nitrate, ammonium and other major ionic species were monitored at 10 locations in southern California (Figure 1) over a 48-hour period. The details of the experiment are described by Russell and Cass (1984), and only will be summarized here.

Gaseous nitric acid and ammonia and the major ionic aerosol species were measured over two hour and four hour intervals using filter-based techniques. Nitric acid measurements used in this study were obtained by the dual filter method, using a teflon prefilter (Membrana Zefluor, 47 mm dia, 1 μm pore size) for aerosol removal, followed by a nylon filter (Ghia Nylasorb, 47 mm dia., 1 μm pore size) that quantitatively collects nitric acid as nitrate (Spicer and Schumacher, 1979; Appel et al., 1980; Spicer et al., 1982). Ammonia was collected as ammonium using an oxalic acid impregnated glass fiber filter (Gelman AE) preceded by a separate teflon prefilter that removed aerosol NH_4^+ (Yoong, 1981; Appel et al., 1980; Cadle et al., 1982). Aerosol phase constituents were measured from material collected on the two teflon prefilters. Ion chromatography was used to determine $\text{SO}_4^{=}$, NO_3^- , Cl^- , Na^+ , and K^+ concentrations. Divalent cations, Ca^{++} and Mg^{++} , were analyzed using atomic absorption spectroscopy (Varian Techtron Model AA6). Ammonium ion concentrations were measured by the phenol hypochlorite method (Salorzano, 1967; Harwood and Kuhn, 1970; Russell, 1983).

EQUILIBRIUM CALCULATIONS

Several alternative methods were used to calculate the partial pressures of ammonia and nitric acid vapor that in theory should be found in equilibrium with the aerosol phase. When the aerosol phase was assumed to consist of pure ammonium nitrate (s or aq) or an aqueous NH_4^+ , NO_3^- , $\text{SO}_4^{=}$ mixture, the calculations were based on the studies by Stelson and Seinfeld (1982a,c). Calculations involving dry, internally-mixed NH_4^+ , NO_3^- , $\text{SO}_4^{=}$ aerosols can be viewed from two perspectives. If the solid phase is assumed to exist as a solid solution, then calculations can be performed by the method of Saxena et al. (1983). If the solid phase exists as a heterogeneous mixture of various crystalline phases, then the vapor pressures could be as high as over solid NH_4NO_3 (Stelson and Seinfeld, 1982c). Each of these approaches is based on fundamental thermodynamic concepts, and provides a method for calculating the equilibrium partial pressure product of NH_3 and HNO_3 that should be found in the presence of a specified level of gaseous and aerosol constituents. The algorithm outlined by Russell et al. (1983) was used to check the apportionment of measured total nitrate ($\text{HNO}_3(\text{g})$ plus NO_3^-) and total ammonia ($\text{NH}_3(\text{g})$ + NH_4^+) between the gaseous and aerosol phases.

Because it is important to an understanding of the data analysis that follows, the mechanics of the aerosol equilibrium model calculations will be described here in some detail, illustrated for the case of pure NH_4NO_3 formation. First, the equilibrium dissociation constant, K , for pure ammonium nitrate is calculated from the ambient

temperature, (T), and relative humidity, (RH) (Stelson and Seinfeld, 1982a). Then the total nitrate, [TN], and total ammonia, [TA], available to form ammonium nitrate is calculated as

$$[\text{TN}] = [\text{HNO}_3(\text{g})]_{\text{m}} + [\text{NO}_3^-]_{\text{m}} \quad (1)$$

$$[\text{TA}] = [\text{NH}_3(\text{g})]_{\text{m}} + [\text{NH}_4^+]_{\text{m}} \quad (2)$$

where $[\text{HNO}_3(\text{g})]_{\text{m}}$ is the measured gaseous nitric acid concentration, $[\text{NH}_3(\text{g})]_{\text{m}}$ is the measured gaseous ammonia concentration, and $[\text{NO}_3^-]_{\text{m}}$ and $[\text{NH}_4^+]_{\text{m}}$ are the measured aerosol nitrate and ammonium concentrations, respectively, available or free to form NH_4NO_3 . Then the equilibrium constraint $[\text{NH}_3(\text{g})][\text{HNO}_3(\text{g})] \leq K$ is imposed. If $[\text{TN}][\text{TA}] \leq K$, no ammonium nitrate is predicted to be present because there is not enough total nitrate and total ammonia to support aerosol NH_4NO_3 formation. If $[\text{TN}][\text{TA}] > K$ then aerosol ammonium nitrate is predicted to form from the gas phase precursors such that the product $[\text{NH}_3(\text{g})]_{\text{c}} [\text{HNO}_3(\text{g})]_{\text{c}} = K$. The subscript c indicates a theoretically computed pollutant concentration that may differ from measured values. Conservation of TA and TN gives the final expression for the ammonium nitrate formed as

$$[\text{NH}_4\text{NO}_3]_{\text{c}} = \frac{[\text{TA}] + [\text{TN}] - \sqrt{([\text{TA}] + [\text{TN}])^2 - 4([\text{TA}][\text{TN}] - K)}}{2} \quad (3)$$

and the gas phase concentrations

$$[\text{NH}_3(\text{g})]_{\text{c}} = [\text{TA}] - [\text{NH}_4\text{NO}_3]_{\text{c}} \quad (4)$$

and

$$[\text{HNO}_3(\text{g})]_{\text{c}} = [\text{TN}] - [\text{NH}_4\text{NO}_3]_{\text{c}} \quad (5)$$

Thus the inputs to the model calculation are TA, TN, T and RH, and the outputs are the calculated aerosol and gas phase concentrations, and the dissociation constant, K. K and the calculated concentrations are very sensitive to T, and also to RH if the RH is high (Figure 2).

Addition of ammonium sulfate to solutions containing aqueous ammonium nitrate would lower the vapor pressure product of $[\text{NH}_3] \times [\text{HNO}_3]$ in equilibrium with the aerosol phase (Figure 2). In Figure 2, Y is the ionic strength fraction of ammonium nitrate and is calculated as

$$Y = \frac{[\text{NH}_4\text{NO}_3]}{[\text{NH}_4\text{NO}_3] + 3[(\text{NH}_4)_2\text{SO}_4]} \quad (6)$$

Note that the concentration product of nitric acid times ammonia in equilibrium with a mixed sulfate/nitrate solution having a value of $Y = 0.5$ is about half as high as that in equilibrium with a pure ammonium nitrate solution. The temperature dependence of the partial pressure product for the aqueous mixed salt case should be similar to that of the pure salt. In the case of a dry internally mixed ammonium nitrate and sulfate solid solution, the vapor pressure product is given as

$$[\text{NH}_3] [\text{HNO}_3] = z K \quad (7)$$

where z is the mole fraction NH_4NO_3 in the aerosol phase and K is the dissociation constant for ammonium nitrate (Saxena et al., 1983). If the dry mixed salt is viewed as a combination of the stable NH_4^+ , NO_3^- , SO_4^{2-} salts, such as NH_4NO_3 and $3(\text{NH}_4\text{NO}_3) \cdot (\text{NH}_4)_2\text{SO}_4$, then the

concentration product of $[\text{NH}_3][\text{HNO}_3]$ at equilibrium with the solid phase could be as high as K calculated for pure NH_4NO_3 (Stelson and Seinfeld, 1982c).

UNCERTAINTY ANALYSIS

Uncertainties arise in this analysis from a number of sources and are important when comparing the theoretically computed pollutant concentrations to the field experimental results. For those cases where the gas phase is assumed to be in equilibrium with pure ammonium nitrate, a formal error analysis was conducted.

An estimate was provided for the standard error of each of the measured parameters required in the calculation: NH_3 , NH_4^+ , HNO_3 , NO_3^- , T and RH . Uncertainties associated with the Gibbs free energies involved in calculations by the method of Stelson and Seinfeld (1982a) were taken from Parker et al. (1976).

The global sensitivity of the calculation scheme to uncertainties in the input variables is very non-linear, and analytical methods for calculating the standard error associated with the model outputs are difficult to execute. Instead, a stochastic simulation approach was used to propagate the error estimates for the measured quantities and Gibbs free energies through the equilibrium calculations. For each time interval at all air sampling sites, the modified Box-Mueller method (Jansson, 1966) was used to generate 200 random, normally distributed, perturbed values for the model input parameters, each set

having a mean equal to the nominally measured parameter value and a standard deviation associated with the uncertainty in that value. Then 200 alternative values for K were calculated and 200 estimates of the partition of TN and TA between the gaseous and aerosol phase were generated using the perturbed data sets. In the figures that follow, error bounds shown represent one standard error about the nominally measured or computed value based on the error propagation study just described. In most cases, uncertainty in the ambient temperatures is the principal contributor to uncertainty in the computed value of the equilibrium dissociation constant, K.

Additional potential contributors to uncertainty in this analysis can be noted, but were not quantified. No attempt was made to include the contribution from uncertainties in thermodynamic properties other than the Gibbs free energies. The additional uncertainty due to the other thermodynamic properties involved in the calculations, such as the molal heat content, osmotic coefficient, ionic activity and specific heats, should be small. The equilibrium between nitric acid, ammonia, water vapor and the aerosol is assumed to prevail at a single instant in time, but calculations were actually based on concentrations and temperatures averaged over 2-hr and 4-hr intervals. It can be shown that if the ambient nitric acid and ammonia concentrations are positively correlated, then the product of the averaged concentrations is less than the averaged concentration product,

$$\overline{P_{\text{HNO}_3}} \overline{P_{\text{NH}_3}} < \overline{P_{\text{HNO}_3} P_{\text{NH}_3}} \quad (8)$$

for any finite time period. Since the extent of this bias is unknown, it was not included in the error analysis. The duration of the sampling interval may also affect the extent of artifact nitrate formation (Appel et al., 1980; Spicer and Schumacher, 1979). It will be seen in the figures that follow that generally better agreement is obtained between theory and experiment when the shorter-term (2-hr) samples are used rather than the longer-term (4-hr) samples.

CASES EXAMINED

Models for ionic aerosol formation in equilibrium with gas phase precursors have been developed only for a limited range of aerosol chemical compositions. The most advanced treatments at present are for concentrated mixed salt solutions containing different combinations of nitrate, sulfate, ammonium, hydrogen and magnesium ions (Saxena et al., 1983; Tang, 1980; Bassett and Seinfeld, 1983). The actual aerosol is much more complex than is assumed by current theoretical models. Results from the present experiment show that the ionic portion of the bulk aerosol contains all of the above, plus sodium, potassium, calcium and chloride ions (see Figures 4 and 5 of Russell and Cass, 1984). From the experimental data, it is impossible to tell how the individual aerosol particles are speciated. In other words, it is not known what fraction of the nitrate or ammonium, if any, is present as ammonium nitrate, and whether the ammonium nitrate is associated with ammonium sulfate (for example) within individual aerosol particles. As a result, three hypothetical distributions of aerosol constituents between particles will be discussed that span the likely range of

aerosol composition: a purely external mixture, a purely internal mixture, and a size-segregated internal mixture.

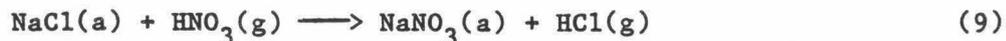
In an external mixture, each particle is composed of a single salt (possibly aqueous) such as pure NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$ or NaCl , and the bulk aerosol composition (as seen in Figures 4 and 5 of Russell and Cass, 1984) is achieved by dispersing a variety of particles with different chemical compositions in the same air mass. At the other extreme, an internal mixture is achieved if each particle has the same chemical composition as the bulk aerosol, and hence consists of a complex mixture of many different anions and cations.

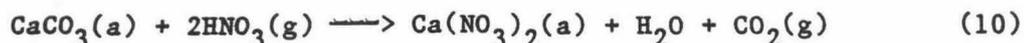
An interesting and intermediate case is that of a size-segregated internal mixture. In this case, the aerosol will be assumed to exist in two size classes, coarse (particle diameter, d_p , $> 2.5 \mu\text{m}$) and fine ($d_p < 2.5 \mu\text{m}$). Coarse aerosols usually are generated mechanically. Sea spray and soil dust aerosols would be prime examples. Gas-particle reactions may take place on the surface of coarse particles, altering the original composition of the aerosol, but the particle size would not decrease significantly. Ionic species concentrated in the large particle fraction would include chiefly, calcium, magnesium, potassium, sodium and chloride, plus enough large particle nitrate to achieve a charge balance (obtained by reaction of nitric acid with sea salt or soil dust). The fine particle fraction will be assumed to have been formed by gas to particle conversion processes, and would contain all of the ammonium, all of the sulfate and that portion of the nitrate not attributed to the coarse particle mode. This framework for the

size-segregated internal mixture hypothesis is consistent with observations that sulfate and ammonium are found chiefly in the small particle size ranges; sodium, calcium and chloride are found in large particles, while nitrate is found in significant amounts in both the coarse and fine fractions (Appel et al., 1978; Kadowaki, 1977).

EXTERNAL MIXTURE

In the case of an external mixture, pure salt particles, such as NH_4NO_3 , NaCl , or $(\text{NH}_4)_2\text{SO}_4$, are assumed to be present, and the gas phase concentrations of NH_3 and HNO_3 are governed by equilibrium with NH_4NO_3 . The key remaining question centers on the possibility that other nitrate containing aerosol species less volatile than NH_4NO_3 are present in separate particles (e.g. NaNO_3), and hence some of the aerosol nitrate is not available to interact with the precursor gases. Field experimental measurements do not give an absolute answer to this question, but two extreme possible cases can be studied. In the first case, all of the ammonia, nitric acid, and aerosol ammonium and nitrate are assumed to be available to form NH_4NO_3 . This provides an upper limit on the amount of pure NH_4NO_3 that can be formed. A second case provides the lower limit on the predicted pure ammonium nitrate concentration by assuming that the nitrate ion is bound preferentially as a relatively non-volatile salt of calcium, magnesium, potassium, or sodium. A number of displacement reactions would bind nitrate in this manner, such as





where (a) indicates the aerosol phase. NaNO_3 has been identified in field measurements in the Los Angeles area (Mamane and Pueschel, 1980). In this study the term FREE NITRATE will be used to identify the fraction of the aerosol nitrate in excess of that which could be bound with the alkali metals or alkaline earths, given mathematically for this experiment as:

$$[\text{FREE NITRATE}] = [\text{NO}_3^-] - \{2[\text{Ca}^{++}] + 2[\text{Mg}^{++}] + [\text{K}^+] + [\text{Na}^+] - [\text{Cl}^-]\} \quad (11)$$

where the brackets ([...]) indicate the measured ionic aerosol concentration in $\mu\text{moles}/\text{m}^3$. The FREE NITRATE concentration was constrained to be greater than or equal to zero. In constructing Equation (11) it was assumed that the chloride ion present is found as sodium chloride. The HCl produced by reaction (9) might, in some cases, react with NH_3 to form NH_4Cl , and thus alternative forms of Equation (11) could be hypothesized.

The choice between the two types of external mixtures just described has no effect on the calculated equilibrium dissociation constant of ammonium nitrate, as K is solely a function of T and RH , but it does affect the calculated gas and aerosol phase pollutant concentrations. If pure ammonium nitrate is present and is at equilibrium with the gas phase, then the equilibrium dissociation constant should be equal to the observed partial pressure product of NH_3 times HNO_3 to within experimental and calculation uncertainties. If the FREE NITRATE concentration is zero, then ammonium nitrate may not be present, and the calculated dissociation constant has no bearing on the partial pressure of ammonia and nitric acid gas, except that it should act as an upper bound on the measured concentration product, CP .

Given the external mixture hypotheses, the theoretically predicted partition of measured total nitrate and total ammonia between the aerosol and gas phases was computed at each monitoring site shown in Figure 1 over each sampling interval during the period August 30-31, 1982. Results at three locations in the basin will be discussed in detail: a near coastal site, Long Beach, a mid-basin site, Anaheim, and a far inland site, Rubidoux. Data on aerosol speciation at these sites are presented elsewhere (Russell and Cass, 1984). The Long Beach sampling station, which is located about 6 km from the Pacific Ocean, experienced lower temperatures (down to 18°C) and higher relative humidities (one hour average above 90%) than the inland sites. This led to a minimum two-hour average calculated NH_4NO_3 dissociation constant of less than 0.75 ppb^2 . Rubidoux, located about 60 km inland, was typically hotter and dryer, with peak temperatures above 38°C, and a correspondingly high calculated dissociation constant that exceeded 650 ppb^2 over one 2-hr sampling interval. Comparison between theory and experiment thus will be discussed for dissociation constants varying over about 3 orders of magnitude.

The calculated NH_4NO_3 dissociation constant, K, and the product of the measured $\text{HNO}_3(\text{g})$ and $\text{NH}_3(\text{g})$ concentrations at Anaheim are shown in Figure 3. One standard error about each calculated value of K is given by the vertical bars, while the standard error of the measured concentration product is indicated by the dashed horizontal lines. Agreement between the theoretical calculations and measurements generally is good, especially for the second day when shorter sampling intervals

were used. Recall that the calculated dissociation constant should serve as an upper bound on the concentration product, CP.

In the first of the two external mixture cases considered, all of the aerosol nitrate is assumed to be present as ammonium nitrate. Given the time history of the computed dissociation constant, the measured total inorganic nitrate and total ammonia concentrations at Anaheim were apportioned between the gaseous and the aerosol phase in accordance with the equilibrium calculations. As seen in Figures 4a and 4b, the measured gas phase concentrations are somewhat below the predicted concentrations, but still are in good agreement given the results of the uncertainty analysis. The calculated and measured aerosol concentrations likewise are in good agreement at Anaheim (Figures 4c and 4d). Note that at a number of times (e.g. between 0800 and 1200 hours on August 30) no ammonium nitrate was predicted to be present. In this case there was not enough total ammonia and total nitrate to support the formation of pure ammonium nitrate at the prevailing ambient conditions.

Moving further inland to Rubidoux, the agreement between the calculated K and measured CP still is good, with the measured CP, again, usually at or below the theoretical value for K during the midday (Figure 5). At night the measured concentration product often lies slightly above K, but there is very little nitric acid vapor present and thus the nitric acid measurement is prone to larger than usual relative error. Rubidoux is downwind of a large collection of dairy farms, and experiences very high ammonia and ammonium ion

concentrations (as seen in Figures 6b and 6d). Agreement between measured and predicted NH_3 concentrations is quite good at all times. The remaining predicted pollutant concentrations match observations at most times, with the largest exceptions occurring between 1000-1200 hours and between 1400-1600 hours on August 31 (see Figure 6).

At the near-coastal sites, like Long Beach and Lennox, the agreement between calculated dissociation constants and measured concentration products is very poor during the daytime (Figure 7). The measured product of the concentrations of nitric acid vapor and ammonia falls significantly below that expected if the gas phase material were in equilibrium with pure NH_4NO_3 . In Figure 8, it can be seen that the lower than expected concentration product measured in the atmosphere is due mainly to lower nitric acid concentrations than would be expected if aerosol ammonium and nitrate ion concentrations were governed solely by the equilibrium between HNO_3 , NH_3 and NH_4NO_3 . At a number of times in the afternoon of both days sampled, the total nitrate and total ammonia concentrations fall below the level needed to form any ammonium nitrate aerosol, as seen in Figure 8cd. Nevertheless, measurable nitrate and ammonium ion concentrations were observed in the aerosol phase during both afternoons (Figure 8). The likely explanation is that pure ammonium nitrate is not present, but that other nitrate and ammonium containing species are formed. In this case, the second external mixture hypothesis will be examined to determine whether part (if not all) of the nitrate could be bound as a relatively non-volatile salt.

The amount of nitrate ion present at each monitoring site in excess of that that could be bound with Na^+ , Ca^{++} , Mg^{++} , and K^+ was determined. This excess NO_3^- ion, called FREE NITRATE, is defined in equation (11). The HNO_3 , NH_3 , NH_4NO_3 equilibrium calculations then were repeated assuming that only the FREE NITRATE plus an equal amount of ammonium ion was available to equilibrate with the gas phase. Results obtained under this hypothesis at Long Beach are shown in Figure 9. In 15 of the 18 sampling periods, no NH_4NO_3 formation would be predicted and indeed no FREE NITRATE was present. At a sixteenth sampling interval NH_4NO_3 is predicted to be present, and the predicted NO_3^- level matches the observed FREE NITRATE almost exactly. Two of the 18 observations still show that FREE NITRATE was present at times when the $\text{NH}_3 \times \text{HNO}_3$ concentration product was too low to form pure NH_4NO_3 .

Results at the remaining monitoring sites are similar to those at Long Beach. The great majority of the occasions where nitrate aerosol is observed at NH_3 and HNO_3 concentrations too low to form pure NH_4NO_3 occur when the aerosol composition is consistent with the presence of nitrate species other than ammonium nitrate. This is illustrated in Figure 10. Figures 10ab show the NH_3 and HNO_3 concentrations predicted at all stations under the first external mixture hypothesis (that all aerosol nitrate is speciated as NH_4NO_3). A large number of the theoretically calculated HNO_3 concentration values exceed the field observations in that case, indicating that more inorganic nitrate should have been found in the gas phase. When the second external mixture hypothesis is imposed (e.g. some nitrate speciated as NaNO_3 ,

$\text{Ca}(\text{NO}_3)_2$ and other non-volatile salts) then the number of outlying data points is reduced to about 10% of the 180 total observations, as shown in Figure 10d. Agreement between observed and predicted NH_3 gaseous concentrations is fairly good at all times under both external mixture hypotheses, as seen in Figures 10ac. This is because gaseous NH_3 is present in such excess that transfer of NH_4^+ ion from the aerosol into the gas phase will not change gaseous NH_3 levels greatly.

INTERNAL MIXTURE

The aerosol observed at each sampling site could be idealized as a pure internal mixture. In this case each aerosol particle would contain a variety of anions and cations in direct proportion to their ionic abundance in the bulk filter sample. For the conditions observed during this experiment, such an internally mixed aerosol would be much more complex than the mixed sulfate, nitrate and ammonium containing aerosols that can be handled by present theoretical models that describe the equilibrium between aerosol and gas phase constituents. If a complete set of thermodynamic data for the species possible in a highly concentrated mixed NH_4^+ , Na^+ , Ca^{++} , Mg^{++} , K^+ , NO_3^- , $\text{SO}_4^{=}$, Cl^- system existed, which it does not, then a general purpose Gibbs free energy minimization technique could provide predictions. Such a technique has been used successfully for the sulfate/nitrate/ammonium system (Bassett and Seinfeld, 1983). Data from the present study can be used to test the predictions of such a complete model once the thermodynamic data for the full system become available. Lacking the

thermodynamic data at present, no attempt will be made to model a purely internal mixture at this time.

SIZE-SEGREGATED INTERNAL MIXTURE

Chemically resolved size distribution measurements show that most of the atmospheric aerosol sulfate and ammonium, and much of the nitrate, is found in a fine particle accumulation mode ($d_p \leq 2.5 \mu\text{m}$), reflecting that they are formed by gas to particle conversion process. Sea salt, soil dust and other mechanically generated aerosols typically are found in a coarse particle mode ($d_p > 2.5 \mu\text{m}$). Any nitrate aerosol formed by reaction of nitric acid with sea salt or soil dust likewise would be concentrated in the coarse particle mode. To capture these characteristics of the atmospheric aerosol, a size-segregated internal mixture hypothesis was tested. The aerosol was assumed to exist in two size fractions for computational purposes. The large particle fraction was taken to be composed of the sea salt and soil dust derived material (all Na^+ , Ca^{++} , Mg^{++} , K^+ , Cl^- and enough NO_3^- to achieve a charge balance) and the fine particle fraction was assumed to contain the sulfate, ammonium and FREE NITRATE in the form of an internally mixed aerosol. Again, the resulting aerosol may be aqueous or solid, for which the calculation methods of Stelson and Seinfeld (1982ac) and Saxena et al. (1983) will be used, as described previously. Both Figure 2 and equation (7) indicate that addition of ammonium sulfate to the internal mixture lowers the resulting vapor pressures in equilibrium with the aerosol phase below the levels observed when pure NH_4NO_3 is present. Thus the size segregated internal mixture hypothesis acts

in the direction needed to account for the few cases in Figure 10d where HNO_3 concentrations are found to be lower than would be expected in equilibrium with NH_4NO_3 alone.

A difficulty arises when considering the size-segregated internal mixture case if no FREE NITRATE is present. If no ammonium nitrate is mixed with the sulfate, the predicted CP goes to zero. At any time when this occurs in the presence of a significant concentration product of ammonia and nitric acid, it will be assumed that the size-segregated internal mixture idealization for the distribution of nitrates between fine and coarse particles is inappropriate. There must have been some nitrate aerosol not bound in a non-volatile form even though ion balance considerations show that all nitrates might have been speciated as non-volatile coarse particle material. No theoretical calculations will be attempted in those cases where the underlying assumption about particle composition is untenable.

The concentration product of HNO_3 and NH_3 calculated for the size-segregated internal mixture case is compared to ambient measurements at Upland in Figure 11 and Long Beach in Table 1. Concentration products that would be predicted for the case of equilibrium with pure NH_4NO_3 also are shown. At Upland, the aerosol is predicted to be aqueous from 0000 hours to 0800 hours and from 2000 to 2400 hours on August 30, and between 0000 and 0800 hours on August 31. The remainder of the time, the aerosol was predicted to be in the solid phase. Results shown in Figure 11b, when the aerosol is solid, are those obtained by the method of Saxena et al. (1983). Alternatively, if the solid mixed salt consists of

a heterogeneous mix of solid phases, such as NH_4NO_3 and $3\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$, then the CP could be as high as for NH_4NO_3 shown in Figure 11a. At Upland the observed and computed concentration products shown in Figure 11b are in better agreement with the size segregated internal mixture case than with the pure external mixture hypothesis in 5 of the cases, particularly those cases with the higher concentration products. In the three cases where improvement is not noted, the absolute value of the discrepancy is only 1 or 2 ppb². At Long Beach, the size-segregated internal mixture hypothesis brings the aqueous phase observation into almost complete agreement between computed and observed concentration products.

CONCLUSION

In theory, the equilibrium dissociation constant for NH_4NO_3 should place an upper limit on the product of the NH_3 and HNO_3 concentrations in the atmosphere. In most cases the $[\text{NH}_3][\text{HNO}_3]$ concentration product measured during this experiment indeed is found to be less than or equal to the calculated dissociation constant of pure NH_4NO_3 at the prevailing conditions. At inland sites like Anaheim and Rubidoux, the assumption that NH_3 and HNO_3 are in equilibrium with pure NH_4NO_3 yields agreement between predicted and measured gas and aerosol phase pollutant concentrations that is qualitatively and, in most cases, quantitatively quite good. At other sites, particularly near the coast, the measured CP and HNO_3 concentrations fall well below those predicted if pure ammonium nitrate is present. A majority of those measurements can be explained by the hypothesis that some nitrate is bound in large

particles by the reaction of nitric acid with sea salt or soil dust. If the aerosol is assumed to exist as a size-segregated internal mixture with nitrates distributed on the basis of ion balance considerations between non-volatile coarse particle material and fine particles containing NH_4^+ , SO_4^{2-} and NO_3^- , then further improvement is obtained between observed and predicted $[\text{NH}_3][\text{HNO}_3]$ concentration products.

The results of this study hold important implications for the construction and use of mathematical models for the formation and transport of nitrate-containing aerosols. First, in the vast majority of cases, measured pollutant concentrations are consistent with computations based on equilibrium between the gas phase and aerosol phase species, to within our present ability to supply the necessary data for the calculations. Given a model like that of Russell et al. (1983) that can compute HNO_3 and NH_3 concentrations from emissions plus gas phase kinetics, in principle it is possible to predict the amount of aerosol nitrate formed. The simplest treatment, that of pure NH_4NO_3 formation, will work well at some monitoring sites, but it is not universally applicable. A knowledge of the speciation of the co-existing non-nitrate ionic material in the aerosol phase is needed if accurate aerosol nitrate concentration predictions are to be made. A formidable problem is faced if that co-existing aerosol concentration and composition also must be computed from emissions data.

Acknowledgement

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FIGURE CAPTIONS

- Figure 1. Air Monitoring Sites in the South Coast Air Basin that Surrounds Los Angeles.
- Figure 2. Partial Pressure Product of Ammonia and Nitric Acid in Equilibrium with a Sulfate, Nitrate and Ammonium Containing Aerosol as a function of Relative Humidity and Ammonium Nitrate Ionic Strength Fraction at 25°C (from Stelson and Seinfeld, 1982c).
- Figure 3. Observed $[\text{HNO}_3][\text{NH}_3]$ Concentration Product and Calculated Dissociation Constant of Pure NH_4NO_3 at Anaheim, CA. No data between 0000 hrs and 0200 hrs on August 31.
- Figure 4. Observed and Calculated Pollutant Concentrations at Anaheim -- External Mixture with all Aerosol Nitrate Available to Form NH_4NO_3 . No data between 0000 hrs and 0200 hrs on August 31.
- (a) HNO_3
 - (b) NH_3
 - (c) NO_3^-
 - (d) NH_4^+
- Figure 5. Observed $[\text{HNO}_3][\text{NH}_3]$ Concentration Product and Calculated Dissociation Constant of Pure NH_4NO_3 at Rubidoux, CA.
- Figure 6. Observed and Calculated Pollutant Concentrations at Rubidoux -- External Mixture with all Aerosol Nitrate Available to Form NH_4NO_3 .
- (a) HNO_3
 - (b) NH_3
 - (c) NO_3^-
 - (d) NH_4^+
- Figure 7. Observed $[\text{HNO}_3][\text{NH}_3]$ Concentration Product and Calculated Dissociation Constant of Pure NH_4NO_3 at Long Beach, CA.
- Figure 8. Observed and Calculated Pollutant Concentrations at Long Beach -- External Mixture with all Aerosol Nitrate Available to Form NH_4NO_3 .
- (a) HNO_3
 - (b) NH_3
 - (c) NO_3^-
 - (d) NH_4^+

Figure 9. Observed and Calculated Pollutant Concentrations at Long Beach — External Mixture with only the FREE NITRATE Available to Form NH_4NO_3 .

- (a) HNO_3
- (b) NH_3
- (c) FREE NITRATE

Figure 10. Comparison of Observed and Calculated Gas Phase Concentrations at all Monitoring Stations under Two Alternative External Mixture Hypotheses (180 Observations).

- Case (1) - All Aerosol Nitrate Available to Form NH_4NO_3 .
- Case (2) - Only the FREE NITRATE Available to Form NH_4NO_3 .
- (a) Ammonia (Case 1)
- (b) Nitric Acid (Case 1)
- (c) Ammonia (Case 2)
- (d) Nitric Acid (Case 2)

Figure 11. Observed and Calculated $[\text{HNO}_3][\text{NH}_3]$ Concentration Product at Upland — Comparison of External Mixture and Size-Segregated Internal Mixture Hypotheses.

- (a) External Mixture
- (b) Size-Segregated Internal Mixture

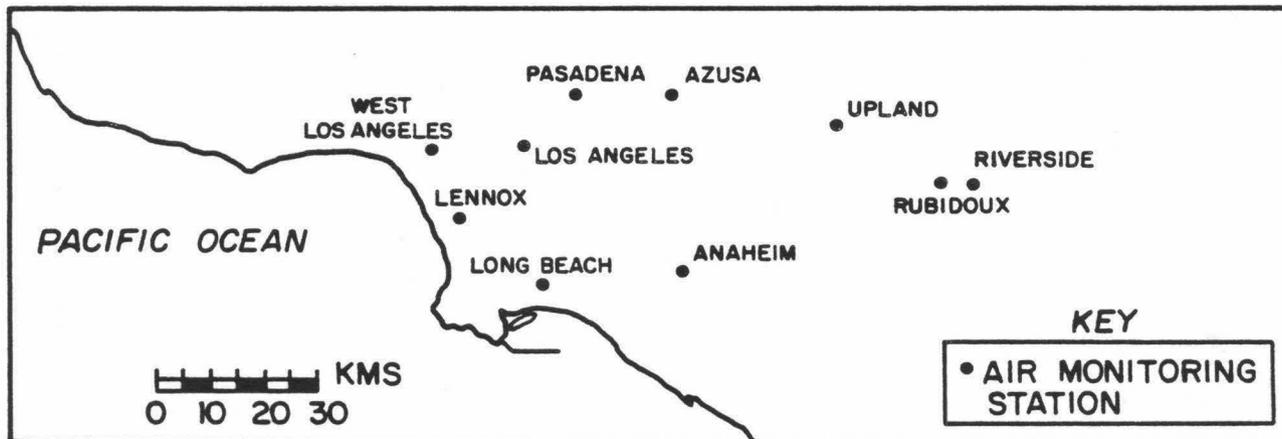


FIGURE 1

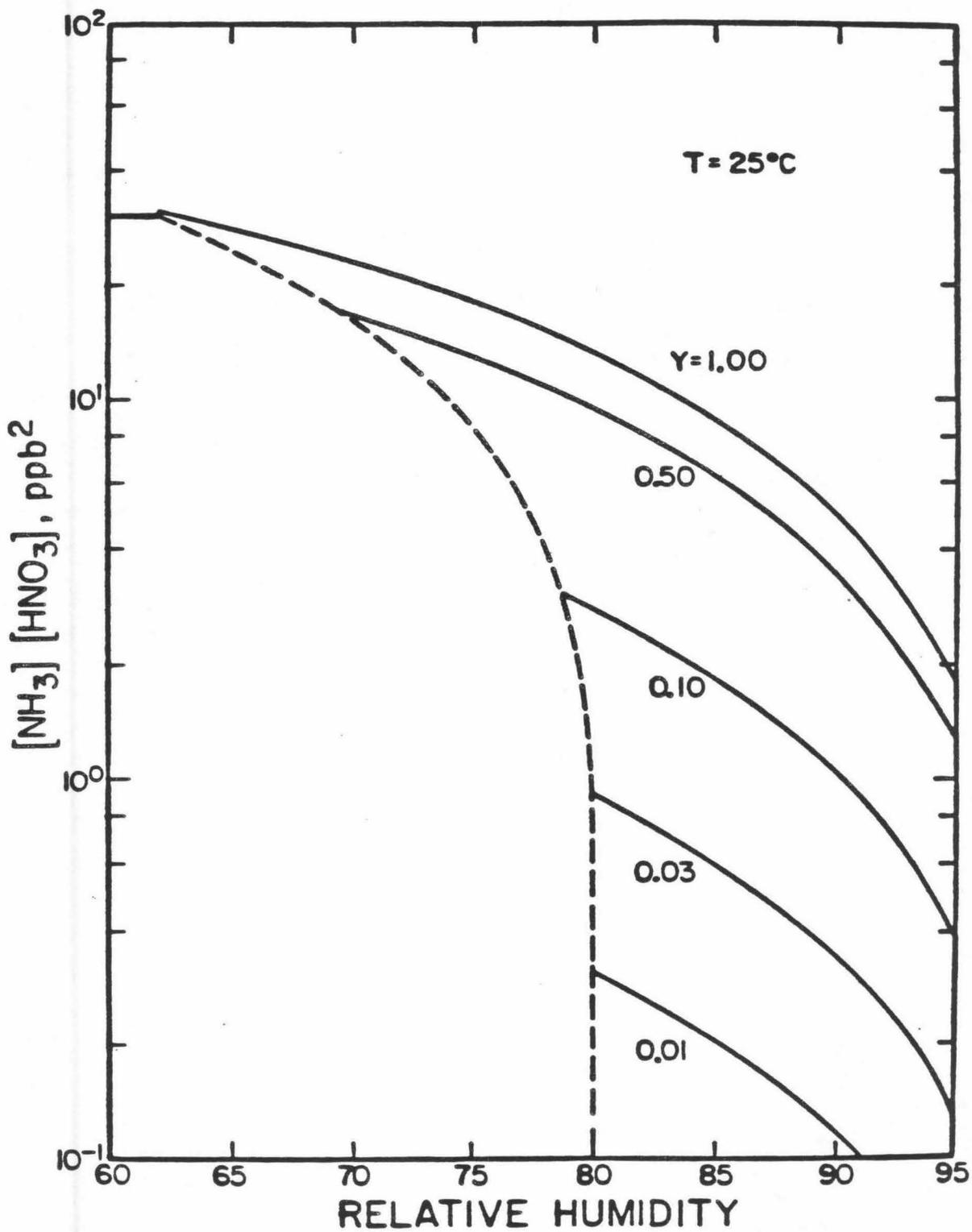


FIGURE 2

CALCULATED DISSOCIATION CONSTANT AND OBSERVED CONCENTRATION PRODUCT
EXTERNAL MIXTURE BASED ON TOTAL NITRATE AND TOTAL AMMONIA

ANAHEIM

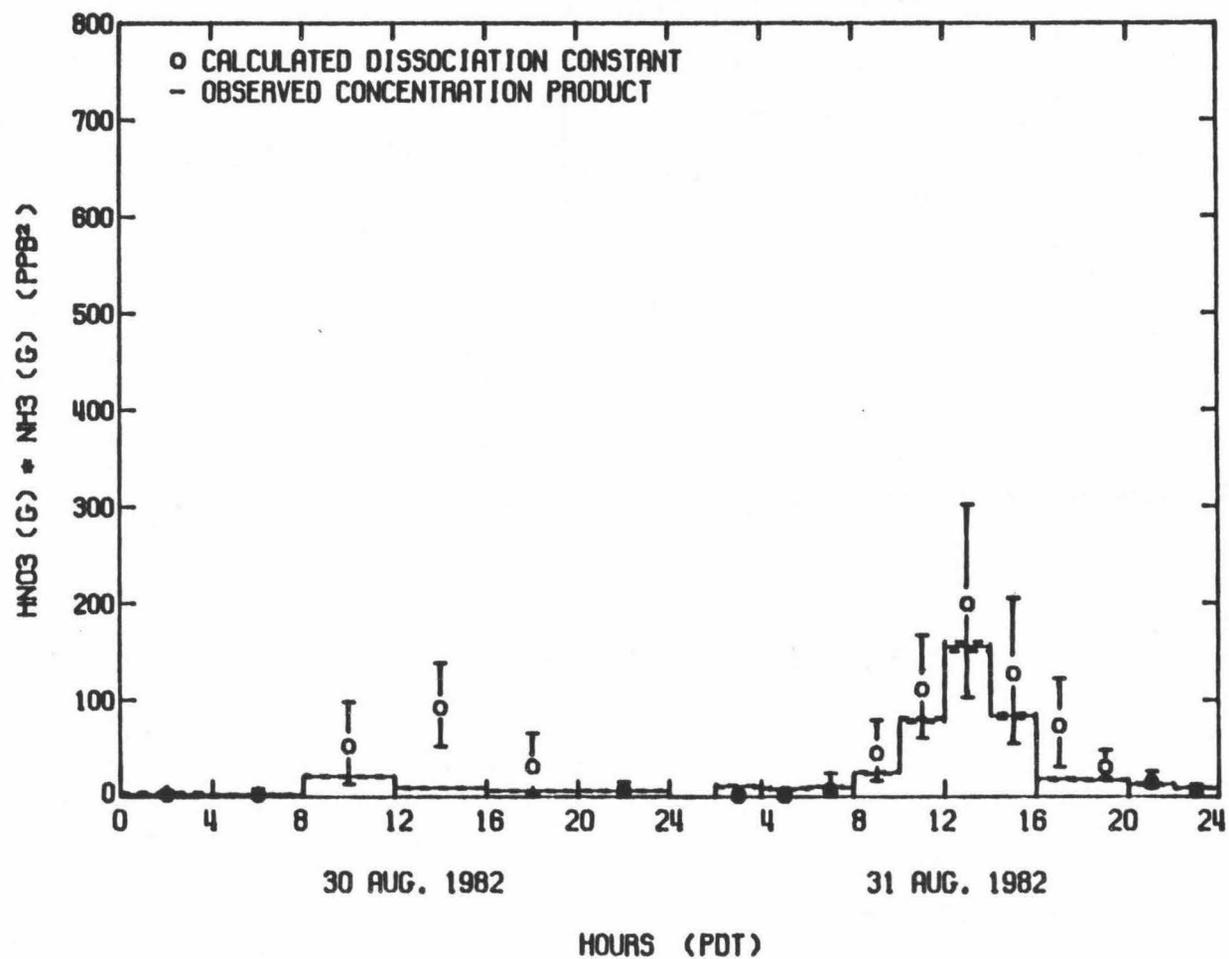
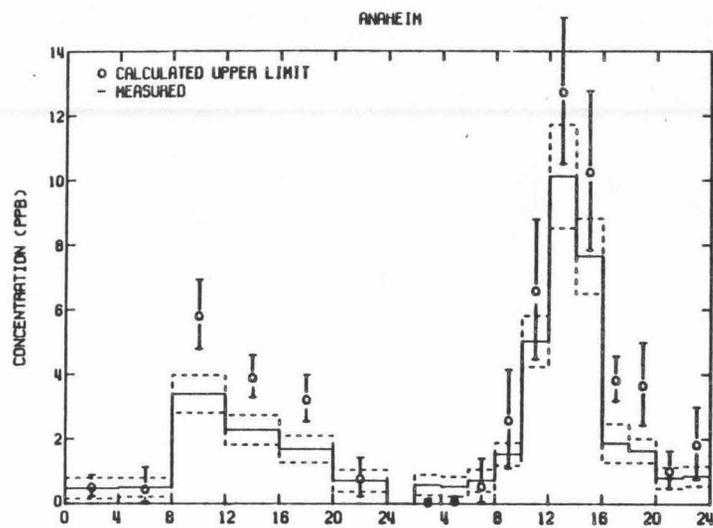


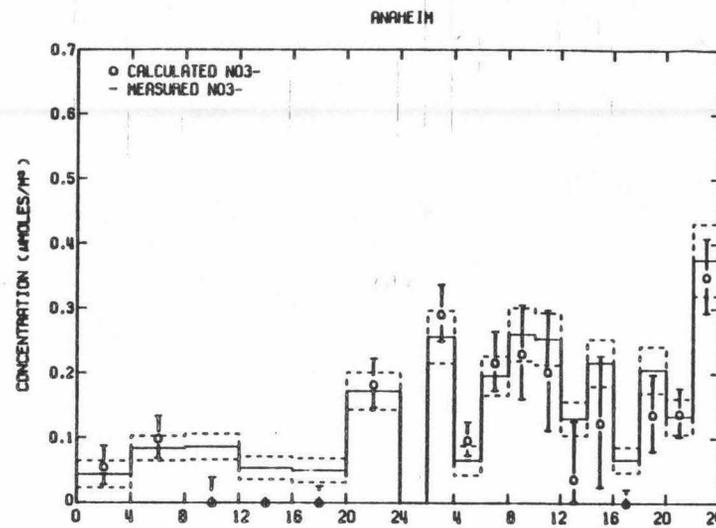
FIGURE 3

CALCULATED UPPER LIMIT ON HNO_3 AND MEASURED HNO_3
EXTERNAL MIXTURE BASED ON TOTAL NITRATE AND TOTAL AMMONIA



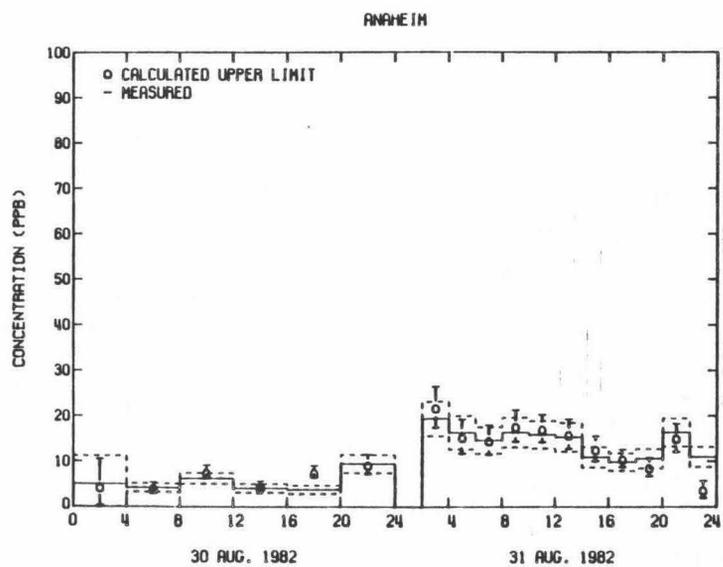
(a)

MEASURED NO_3^- AND NO_3^- CALCULATED IF PURE NH_4NO_3 IS FORMED
EXTERNAL MIXTURE BASED ON TOTAL NITRATE AND TOTAL AMMONIA



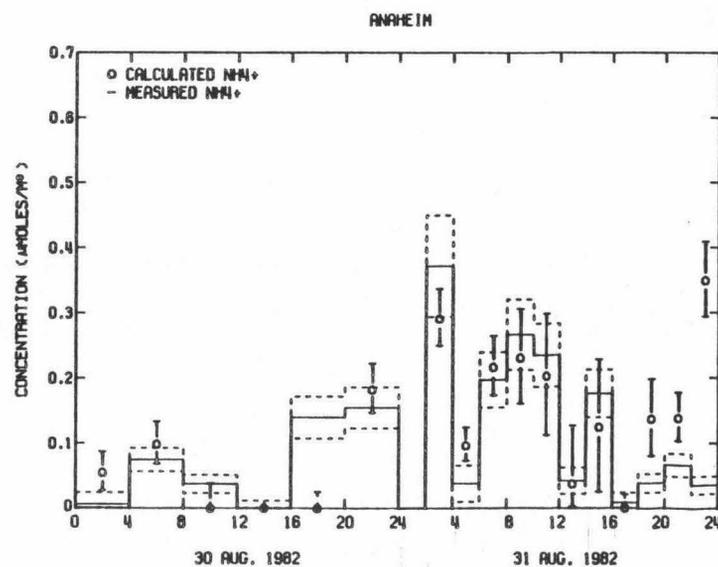
(c)

CALCULATED UPPER LIMIT ON NH_3 AND MEASURED NH_3
EXTERNAL MIXTURE BASED ON TOTAL NITRATE AND TOTAL AMMONIA



(b)

MEASURED NH_4^+ AND NH_4^+ CALCULATED IF PURE NH_4NO_3 IS FORMED
EXTERNAL MIXTURE BASED ON TOTAL NITRATE AND TOTAL AMMONIA



(d)

FIGURE 4

CALCULATED DISSOCIATION CONSTANT AND OBSERVED CONCENTRATION PRODUCT

EXTERNAL MIXTURE BASED ON TOTAL NITRATE AND TOTAL AMMONIA

RUBIDOUX

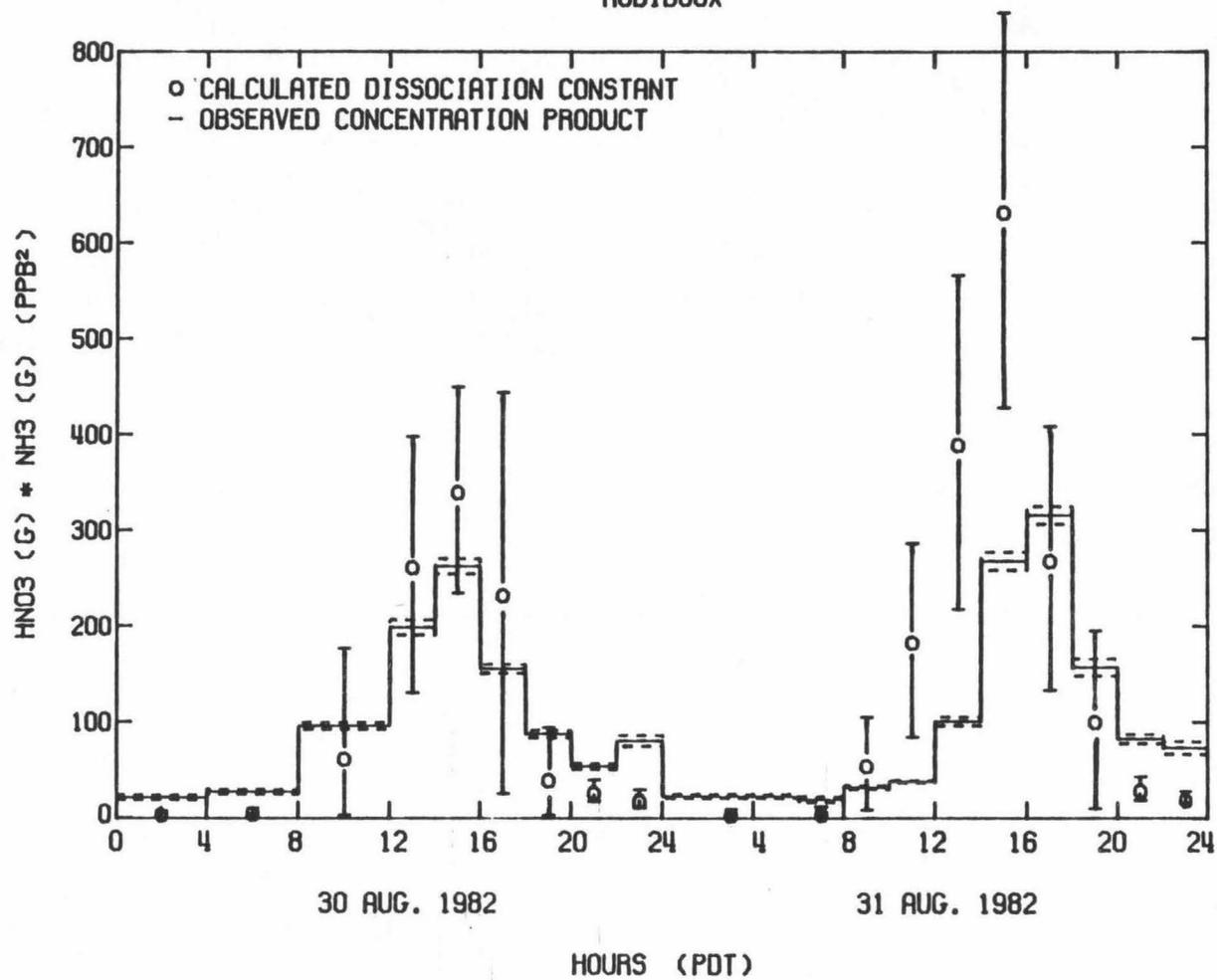
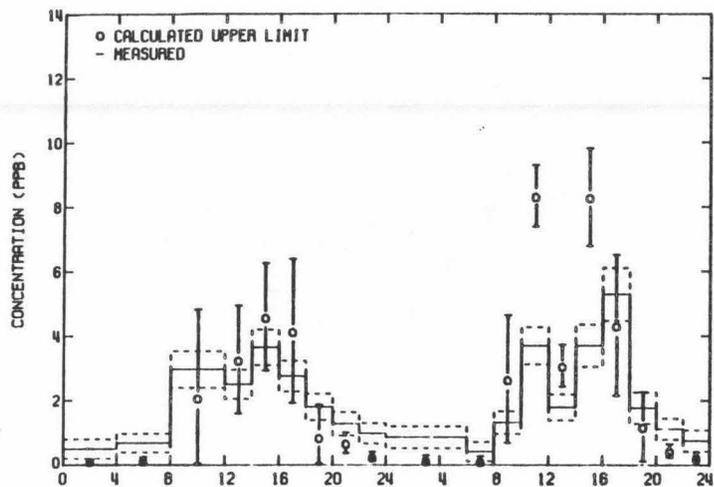


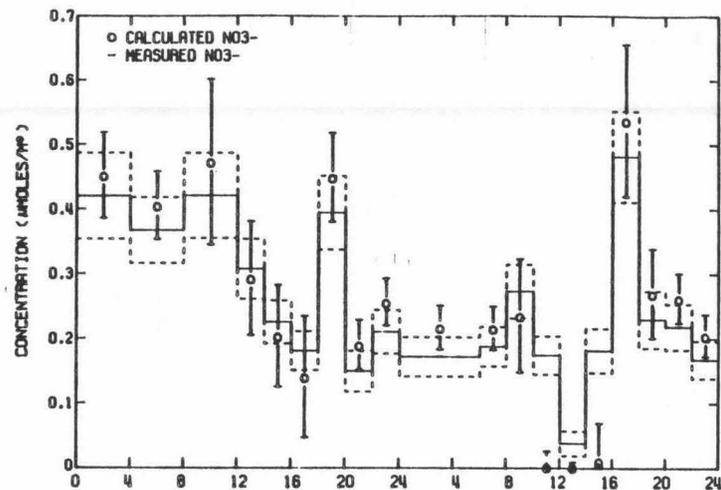
FIGURE 5

CALCULATED UPPER LIMIT ON HNO_3 AND MEASURED HNO_3
 EXTERNAL MIXTURE BASED ON TOTAL NITRATE AND TOTAL AMMONIA
 RUBIDOUX



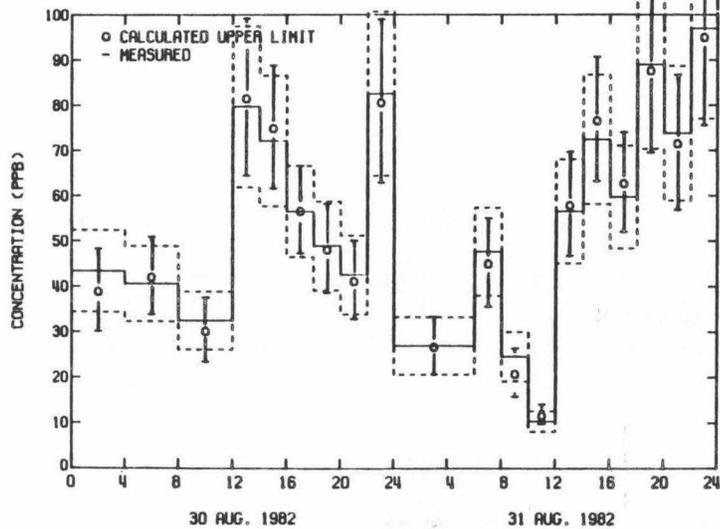
(a)

MEASURED NO_3^- AND NO_3^- CALCULATED IF PURE NH_4NO_3 IS FORMED
 EXTERNAL MIXTURE BASED ON TOTAL NITRATE AND TOTAL AMMONIA
 RUBIDOUX



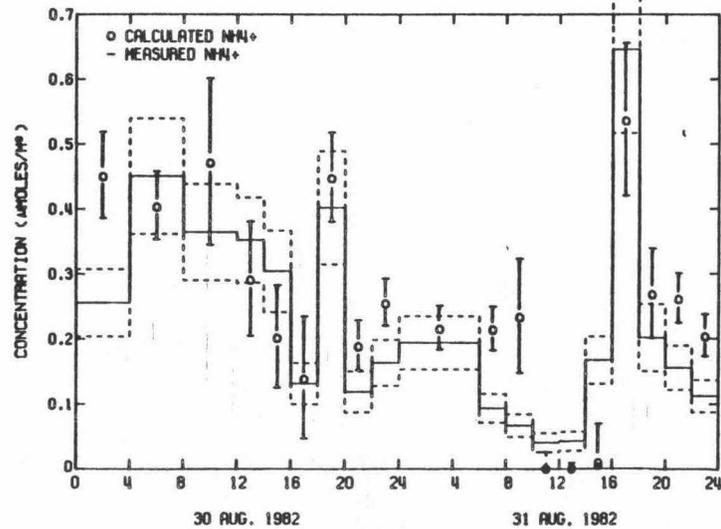
(c)

CALCULATED UPPER LIMIT ON NH_3 AND MEASURED NH_3
 EXTERNAL MIXTURE BASED ON TOTAL NITRATE AND TOTAL AMMONIA
 RUBIDOUX



(b)

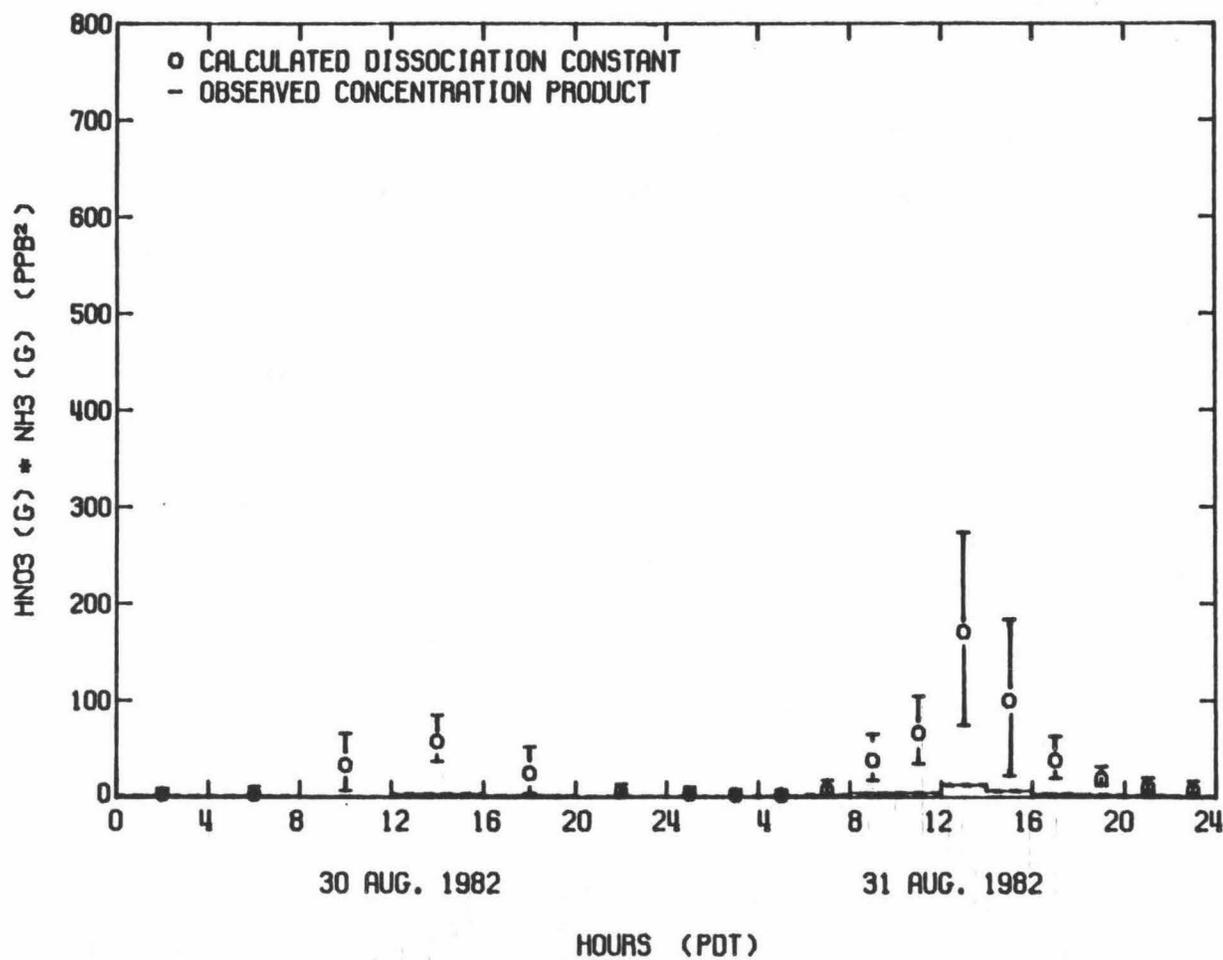
MEASURED NH_4^+ AND NH_4^+ CALCULATED IF PURE NH_4NO_3 IS FORMED
 EXTERNAL MIXTURE BASED ON TOTAL NITRATE AND TOTAL AMMONIA
 RUBIDOUX



(d)

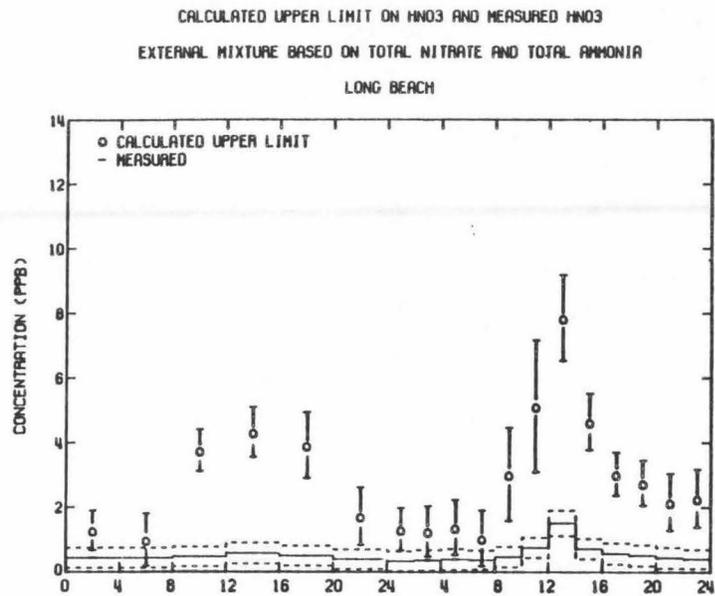
FIGURE 6

CALCULATED DISSOCIATION CONSTANT AND OBSERVED CONCENTRATION PRODUCT
EXTERNAL MIXTURE BASED ON TOTAL NITRATE AND TOTAL AMMONIA
LONG BEACH

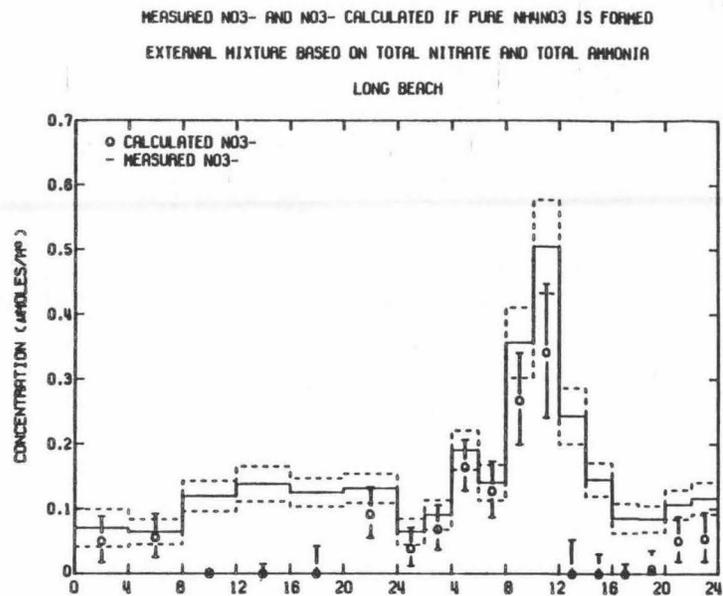


HOURS (PDT)

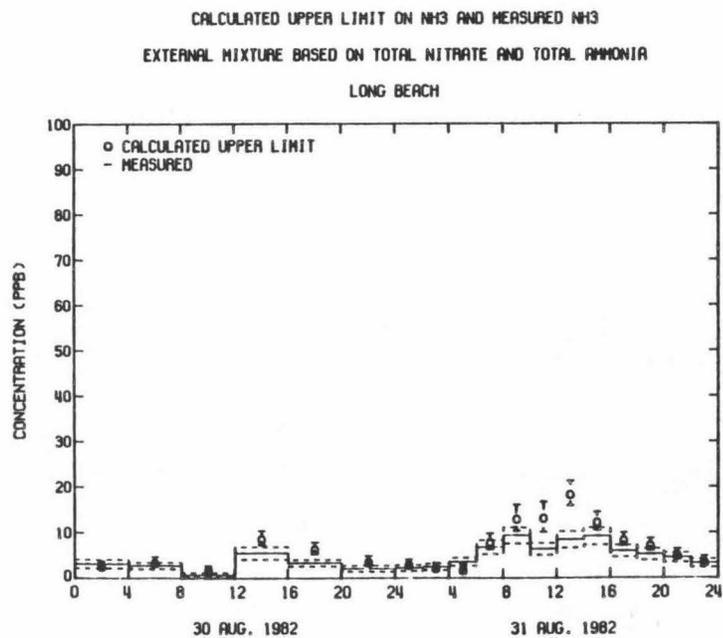
FIGURE 7



(a)

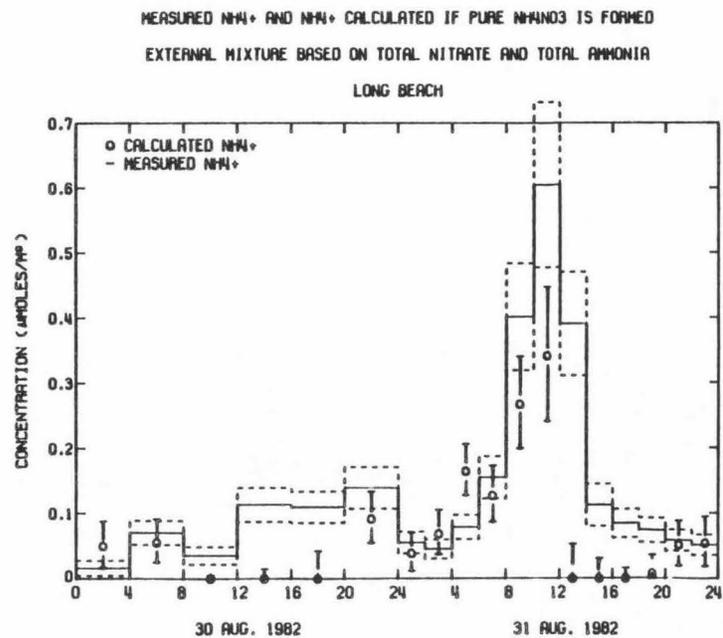


(c)



HOURS (PDT)

(b)

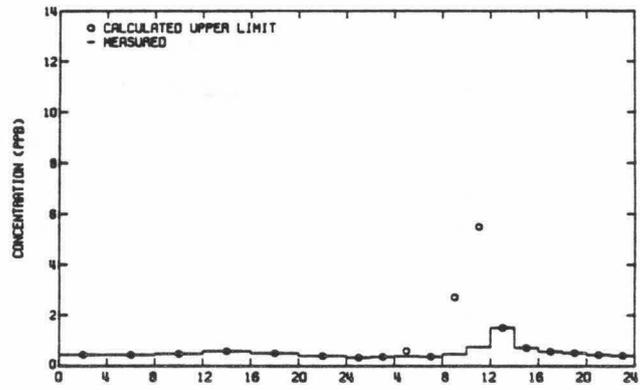


HOURS (PDT)

(d)

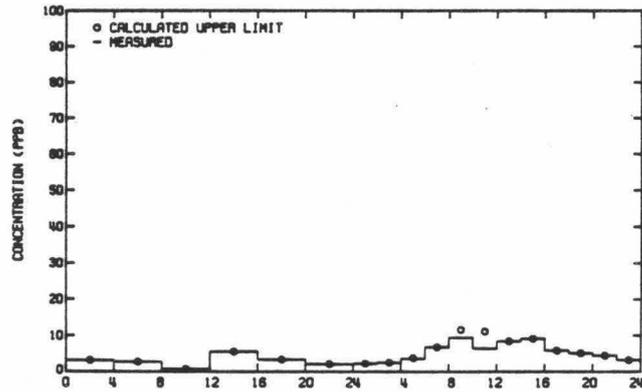
FIGURE 8

CALCULATED UPPER LIMIT ON HNNO_3 AND MEASURED HNNO_3
 EXTERNAL MIXTURE BASED ON FREE NITRATE
 LONG BEACH



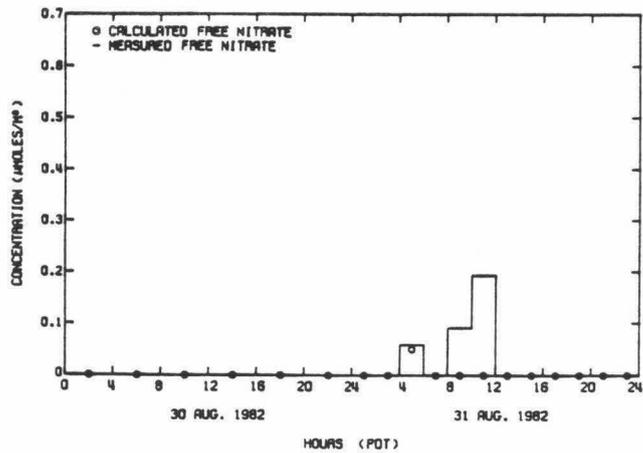
(a)

CALCULATED UPPER LIMIT ON NH_3 AND MEASURED NH_3
 EXTERNAL MIXTURE BASED ON FREE NITRATE
 LONG BEACH



(b)

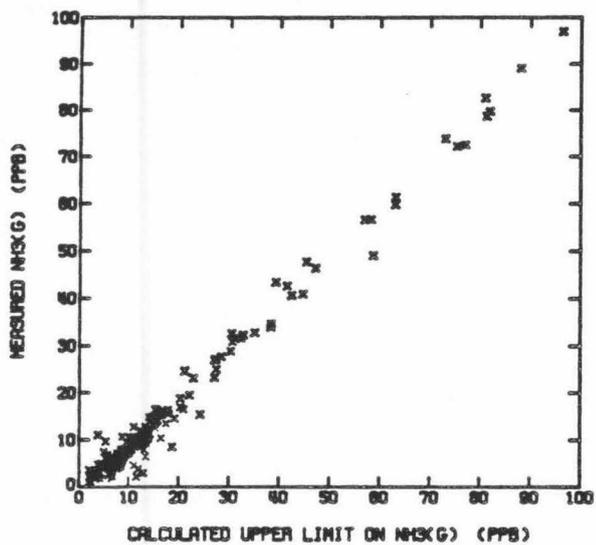
MEASURED FREE NITRATE AND FREE NITRATE CALCULATED IF PURE NH_4NO_3 IS FORMED
 EXTERNAL MIXTURE BASED ON FREE NITRATE
 LONG BEACH



(c)

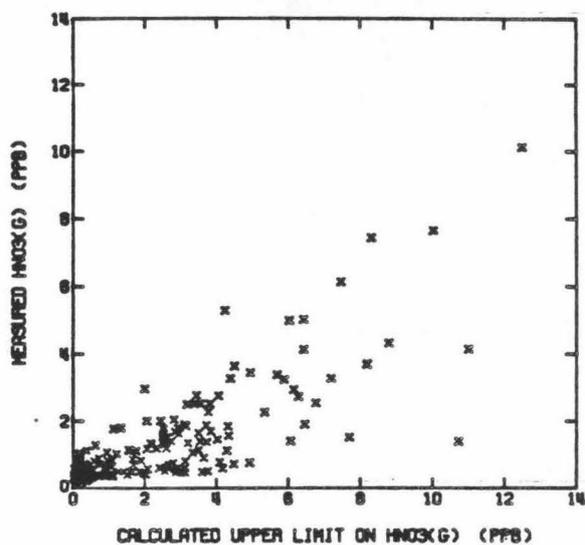
FIGURE 9

CALCULATED UPPER LIMIT ON NH3 VERSUS MEASURED NH3
(SOLID AND AQUEOUS FOR ALL STATIONS)

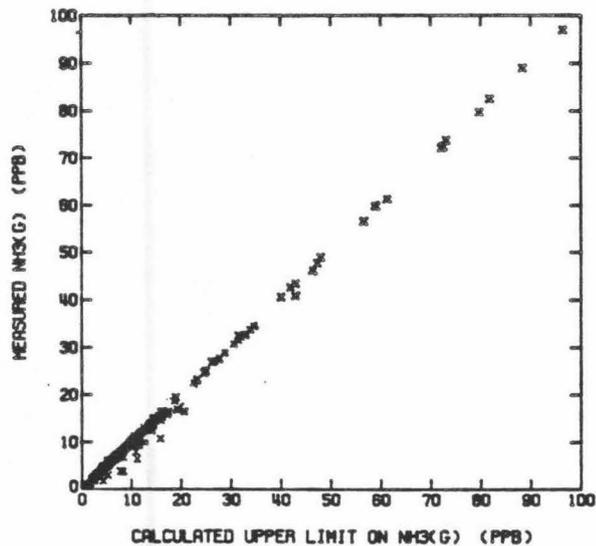


(a)

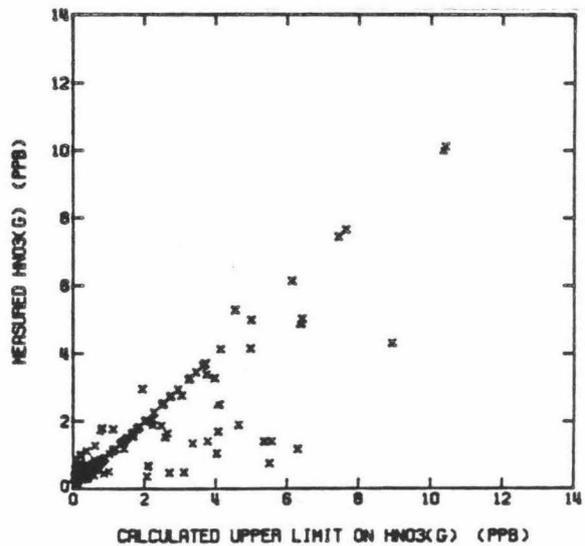
CALCULATED UPPER LIMIT ON HNO3 VERSUS MEASURED HNO3
(SOLID AND AQUEOUS FOR ALL STATIONS)



(b)

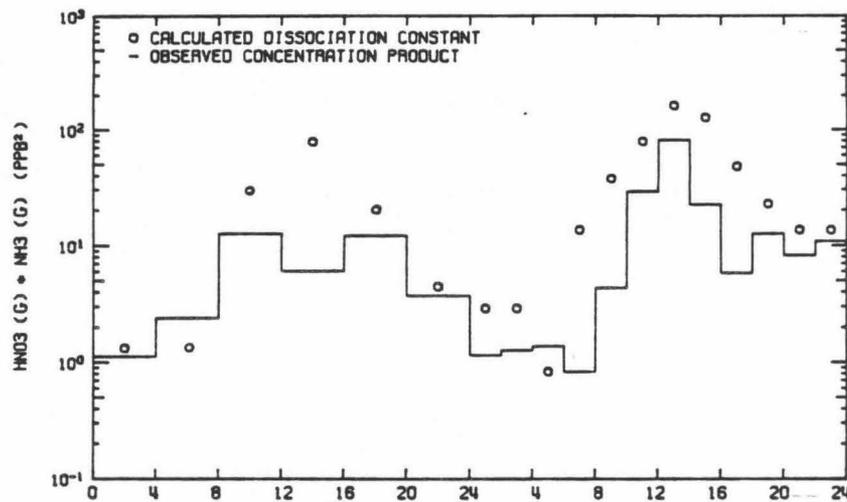


(c)

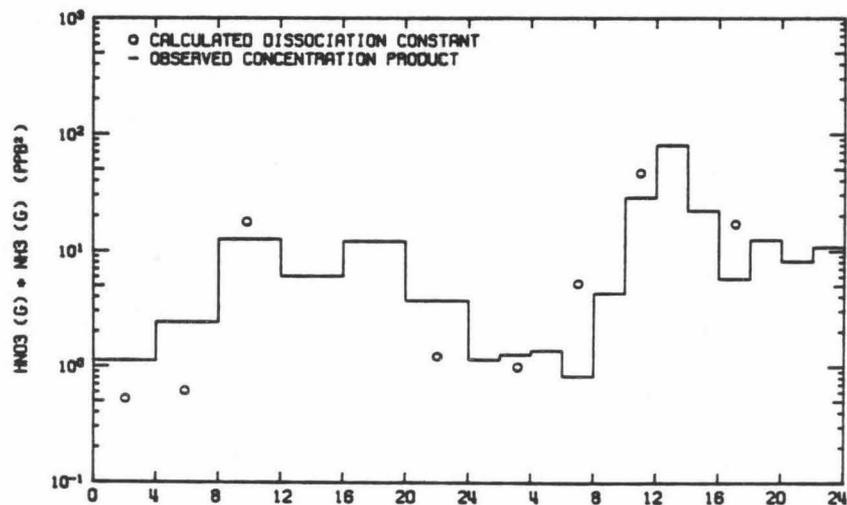


(d)

FIGURE 10



(a)



(b)

FIGURE 11

TABLE 1

Comparison of Measurements at Long Beach to Predictions Given by the
Pure External Mixture Hypothesis Based on FREE NITRATE (Case 1)
and by the Size-Segregated Internal Mixture Hypothesis (Case 2)

TIME*	PHASE [†]	CP (ppb ²)			HNO ₃ (ppb)			NH ₃ (ppb)			FREE NITRATE (µgm/m ³)		
		CASE 1 [†]	CASE 2	MEAS.	CASE 1	CASE 2	MEAS.	CASE 1	CASE 2	MEAS.	CASE 1	CASE 2	MEAS.
4-6	aqueous(aq)	2.6	1.4	1.2	0.6	0.3	0.3	4.3	4.1	4.0	2.6	3.4	3.5
8-10	solid(s)	39.0	9.6	4.5	2.7	1.0	0.5	11.7	9.9	9.5	0.0	4.4	5.9
10-12	solid(s)	69.0	16.0	4.9	5.4	2.1	0.8	11.1	7.7	6.4	0.0	8.4	12.0

* At all other times Case 1, Case 2 and measurements match exactly because no FREE NITRATE is present. All times shown are on August 31, 1983.

[†] When solid, Case 2 is computed by the method of Saxena et al. (1983). For solid particles containing a mixture of solid phases, such as NH₄NO₃ and 3NH₄NO₃ · (NH₄)₂SO₄, CP could be as high as for pure NH₄NO₃ in the Case 1 column.

[†] Values shown are for equilibrium dissociation constant, K, for NH₄NO₃.

This can exceed concentration product of [NH₃][HNO₃] if no FREE NITRATE is predicted to be present.