

Chemical coupling between ammonia, acid gases, and fine particles

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“Capsule”: *Our study of ammonia, acid gases, and fine particles provided a gas-to-particle conversion process that improved prediction of long-range transport of pollutants, air quality, and climate change.*

Abstract

The concentrations of inorganic aerosol components in the fine particulate matter ($PM_{\text{fine}} \leq 2.5 \mu\text{m}$) consisted of primarily ammonium, sodium, sulfate, nitrate, and chloride are related to the transfer time scale between gas to particle phase, which is a function of the ambient temperature, relative humidity, and their gas phase constituent concentrations in the atmosphere. This study involved understanding the magnitude of major ammonia sources; and an up-wind and down-wind (receptor) ammonia, acid gases, and fine particulate measurements; with a view to accretion gas-to-particle conversion (GTPS) process in an agricultural/rural environment. The observational based analysis of ammonia, acid gases, and fine particles by annular denuder system (ADS) coupled with a Gaussian dispersion model provided the mean pseudo-first-order k_{S-1} between NH_3 and H_2SO_4 aerosol $\sim 5.00 (\pm 3.77) \times 10^{-3} s^{-1}$. The rate constant was found to increase as ambient temperature, wind speed, and solar radiation increases, and decreases with increasing relative humidity. The observed $[NH_3][HNO_3]$ products exceeded values predicted by theoretical equilibrium constants, due to a local excess of ammonia concentration.

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1. Introduction

Over the past two decades, the chemical reactions between acidic aerosols and ammonia, called gas-to-particle conversion (GTPS) processes, have been examined (Lenhard and Gravenhorst, 1980; McMurry et al., 1983; Harrison and Kitto, 1992). Ammonia gas is the dominant trace gas capable of neutralizing the acid gases produced by the oxidation of SO_2 and NO_2 in the atmosphere. The soluble ammonium aerosol salts of sulfuric acid (H_2SO_4) and nitric acid (HNO_3) produced by neutralization processes with atmospheric ammonia become atmospheric aerosols in the sub-micron size range (McMurry et al., 1983; Warneck, 2000). The conversion from solid phase to liquid phase occurs only when the relative humidity reaches a certain critical

value corresponding to the water activity of the saturated solution, called Deliquescence of Relative Humidity (DRH) (Tang and Munkelwitz, 1977; Tang, 1980). Gaseous ammonia reacts with gaseous HNO_3 and HCl to form NH_4NO_3 and NH_4Cl , respectively, in a reverse process depending on relative humidity in the atmosphere. Many scientists have examined the complex reversible chemical reactions between nitric acid gas and ammonium salts (Stelson and Seinfeld, 1982a,b; Singneur, 1982; Singneur and Saxena, 1984; Russell et al., 1983; Saxena et al., 1983; Bassett and Seinfeld, 1983; Hilldermann et al., 1984; Pilinis et al., 1987; Pilinis and Seinfeld, 1987; Wexler and Seinfeld, 1992; Kim et al., 1993a,b; Pacyna and Benson, 1996; Seinfeld and Pandis, 1998). Deposition of NH_3 , HNO_3 , and NH_4NO_3 provide important soil nutrients. However, excess input may lead to soil acidification and eutrophication of the ecosystem. Particulate ammonium nitrate can exist either in the gaseous or particulate phase depending on the ambient air temperature, relative humidity, and its aerosol composition in the atmosphere (Cadle, et al.,

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1982). However, because ammonium sulfate aerosol has a low vapor pressure, which allows it to condense easily on particle and droplets surfaces even at low relative humidity, sulfate ions in fine particulate matter are therefore primarily present with ammonium, nitrate, and other mixtures of ammonium salts. The chemical reaction between sulfuric acid and ammonia is the preferred chemical reaction in the atmosphere (Huntzicker et al., 1980; McMurry et al., 1983; Erisman et al., 1988; Harrison and Kitto, 1992; Warneck, 2000). Ammonium bisulfate (NH_4HSO_4) exists over all ranges of relative humidity (Saxena et al., 1986). Huntzicker et al. (1980) and McMurry et al. (1983) measured the reaction rate constant between ammonia gas and sulfuric acid aerosol under certain laboratory conditions. They determined the extent of the neutralization process between H_2SO_4 aerosol and NH_3 gas by comparing the hygroscopic and deliquescent properties of the product aerosols with the known properties of aerosols consisting of internal mixtures of sulfuric acid and ammonium salts, and particle size. Erisman et al. (1988) calculated an average conversion rate between ammonia and ammonium ($1 \times 10^{-4} \text{ s}^{-1}$) for daytime periods and $5 \times 10^{-5} \text{ s}^{-1}$ for nighttime periods based on the vertical observed aerosol distribution. Harrison and Kitto (1992) modified the rate constant by Erisman et al. (1988) by substituting ammonia and ammonium horizontal distribution; and determined a pseudo-first-order rate constant for this reaction within the range $4 \times 10^{-6} \text{ s}^{-1}$ to $4.1 \times 10^{-4} \text{ s}^{-1}$. Both these studies have uncertainties arising (1) vertical inhomogeneity in the boundary layer from Erisman et al., (1988), and large distances between sites, and large sampling periods (24 h) from Harrison and Kitto (1992). Asman and Van Jaarsveld (1990) used a value of $8 \times 10^{-5} \text{ s}^{-1}$ in their long-range transport model for modeling of ammonia and ammonium in Europe. Vermetten et al. (1985) also suggested a value of a rate constant from 10^{-5} to 10^{-3} s^{-1} in the atmospheric boundary (i.e. $\sim 100\text{m}$). Lenhard and Gravenhorst (1980) who estimated the rate constant ($\approx 2.1 \times 10^{-5} \text{ s}^{-1}$) at 400 m heights suggested that greater values for conversion rate might occur at lower elevation levels. All these conversion rate constants are not real rate constants between NH_3 and H_2SO_4 aerosol in the atmosphere but depend on the presence of acidic components in the atmosphere and on the atmospheric mixing characteristics. It could be called the conversion rate of NH_3 to NH_4^+ by all chemical reactions of ammonia with acid gases, such as H_2SO_4 , HNO_3 , HCl , and OH radical.

The experimental aspects of this study involved understanding the gas-to-particle conversion processes in the atmosphere. Our interests in this study were aimed towards the estimation of the kinetic rate constant for the gas-to-particle conversion process. The reaction rate constants of NH_3 with H_2SO_4 , HNO_3 , and

HCl aerosols have been estimated, and compared with other studies. The relationships between the rate constant and meteorological parameters, such as ambient temperature, relative humidity, wind speed, and solar radiation, were also analyzed. The products of NH_3 and HNO_3 concentrations measured in ammonia rich environment (i.e. at a commercial hog farm in eastern NC) are compared to the NH_4NO_3 equilibrium constant derived from equilibrium chemical thermodynamics.

2. Experimental

The study area consisted of two measurement sites (North Farm (NF) and South Farm (SF)) at a swine production facility in eastern North Carolina (Aneja et al., 1997, 2000, 2001). The NF site was located approximately 50 m northeast of a hog waste storage and treatment lagoon, and the SF site was located approximately 400 m south-southwest of the waste lagoon (Fig. 1). Samples were collected using an annular denuder system (ADS) from May to July 1998 at the NF site and from May 1998 to April 1999 at the SF site. For comparison between NF and SF sites, only ADS data from May to July 1998 at both sites were used for this study. The ADS system consisted of a cyclone separator to remove coarse particles greater than $2.5 \mu\text{m}$ diameter, two diffusion denuders in series coated with sodium carbonate and citric acid, respectively, and a

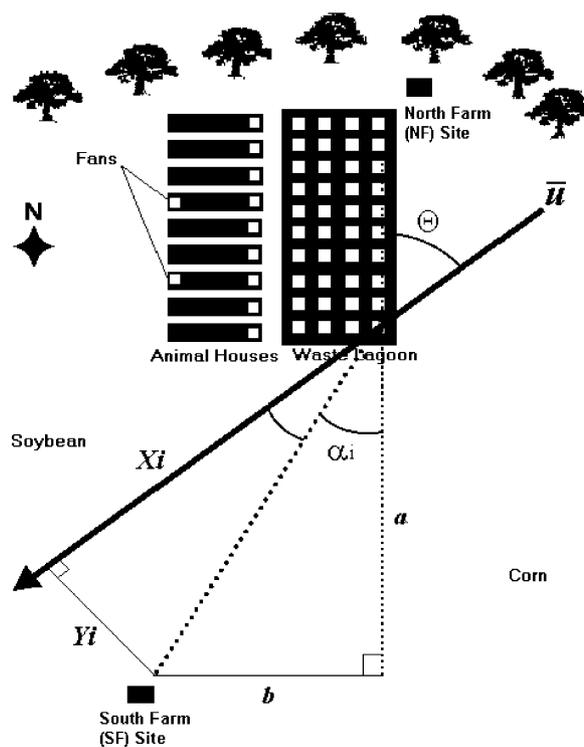


Fig. 1. Layout of a swine lagoon and barns at sampling site wind direction dependent geometric parameters for each point source.

filter pack containing a Teflon and a nylon filter all in series. The sodium carbonate coated denuders yielded average acid gas concentrations of hydrogen chloride (HCl), nitrous acid (HONO), nitric acid (HNO₃), and sulfur dioxide (SO₂). The citric acid coated denuders yielded average concentrations of ammonia (NH₃). The combined Teflon and nylon filters yielded fine aerosol (PM_{≤2.5} μm) concentrations of ammonium (NH₄⁺), chloride (Cl⁻), nitrate (NO₃⁻), and sulfate (SO₄²⁻) ions. The latter nylon filter collects ammonia released from the Teflon filter due to the evaporation of ammonia from ammonium nitrate and ammonium chloride. ADS measurements were conducted over 12-h integrated sampling, representing daytime and nighttime averages. After sampling, the sampler was sealed immediately and extreme care was taken in handling the samples both during transport and inside the laboratory to protect samples from neutralization of acidic particles.

Meteorological parameters were measured at a 10-meter tower near the SF site. Wind direction, wind speed, and air temperatures were measured at both 2 meter and 10 meter elevations. Relative humidity was measured at 2 meters, while solar radiation and precipitation were measured at ground level.

3. Comparisons between NF and SF sites

Aneja et al. (1997, 2000) showed that the total emission of ammonia from commercial hog farms in North Carolina might be as much as approximately 90,000 tons NH₃/year, and that eastern NC, which has a high population density of domestic livestock, especially hogs, has been characterized as being ammonia-rich and having corresponding ammonium aerosols, which are dominated by ammonium sulfates (McCulloch et al., 1998).

Although wind directions could fluctuate to some extent within each sampling period, it was possible to select data with a great predominance in the appropriate wind sector. Fig. 2 summarizes the frequency of ammonia concentration regime by wind direction. During the measurement period, not only the southwest wind was dominant but also higher concentrations of ammonia occurred at the NF site, which is influenced by the nearby waste lagoon. On the other hand, during the northeast wind direction, higher ammonia concentrations occurred at the SF site. Based on the data measured from an ammonia rich agricultural environment, i.e. a commercial hog farm in eastern NC, the constituents of aerosols can be analyzed in a meaningful manner by examining the equivalent ratios of NH₄⁺/SO₄²⁻ and NH₄⁺/NO₃⁻, and NH₄⁺/(SO₄²⁻ + NO₃⁻ + Cl⁻) (Table 1). Equivalent NH₄⁺/SO₄²⁻ ratios are expected to range from 0.5 to 1.0, corresponding to a composition between ammonium bisulfate (NH₄HSO₄) and ammonium sulfate

([NH₄]₂SO₄) (Lee, 1993). Larger observed equivalent NH₄⁺/SO₄²⁻ ratio presented here suggests that this site is dominated by ammonium sulfate due to the predominant ammonia rich environment. Thus, it indicates that all particulate SO₄²⁻, NO₃⁻, and Cl⁻ ions were associated with NH₄⁺ and that some excess ammonium remained, leaving a base-rich environment in the particulate matter.

4. Contributions of NH₃ emission to receptor

Estimation of ammonia contributions from a lagoon and barns to the receptor SF site in the farm could be one of major factors for understanding of gas-to-particle conversion processes between ammonia, acid gases, and fine particle in this study site. To estimate the contribution of ammonia to the receptor, a Gaussian dispersion model was adapted in this study. Ammonia emission from a swine lagoon is estimated by a Coupled Mass Transfer and Chemical Equilibrium Reaction model based on this and several other swine lagoons in the eastern N.C. (Aneja et al., 2001), and used as an ammonia emission input factor for a Gaussian dispersion model. The model emission predictions indicates an exponential increase in ammonia flux with increasing lagoon temperature and pH, a linear increase with increasing lagoon Total Ammoniacal Nitrogen (TAN), and an increase with increasing wind speed. Input parameters for the ammonia flux model, such as lagoon pH 7.7(±0.06), TAN 603.3(±48.2) mg N/l, and lagoon temperature 24.7(±3.2)°C, are obtained from Aneja et al. (2000). Ambient temperature, wind speed at 2 m, and ambient ammonia concentration at this study site are required for estimation of ammonia flux emission. The average estimated ammonia emission from the waste lagoon in this sampling farm is approximately 5.38×10² μg NH₃/m²/min during the measurement periods. The ammonia emissions from swine barn approximately 3.09 kg NH₃/animal/year are conducted from Harris and Thompson (1999).

The Gaussian dispersion model was validated using experimental data and using the experimental and theoretical input parameters, such as stability classes and effective wind speed (Arya, 1999). A stability class is determined by the extended conditions of Pasquill Stability types based on hourly meteorological parameters (Pasquill, 1961). Briggs' interpolation formulas (Briggs, 1973) are used for assigning dispersion parameters, such as σ_y and σ_z, based on Pasquill stability classes (Pasquill, 1961; Turner, 1970). The method of images is used to consider the reflecting surface assumption. This implies an image source below the surface to account for the increased concentration in the plume, and a perfectly reflecting surface, such that all mass emitted is contained within the plume, and therefore there is no

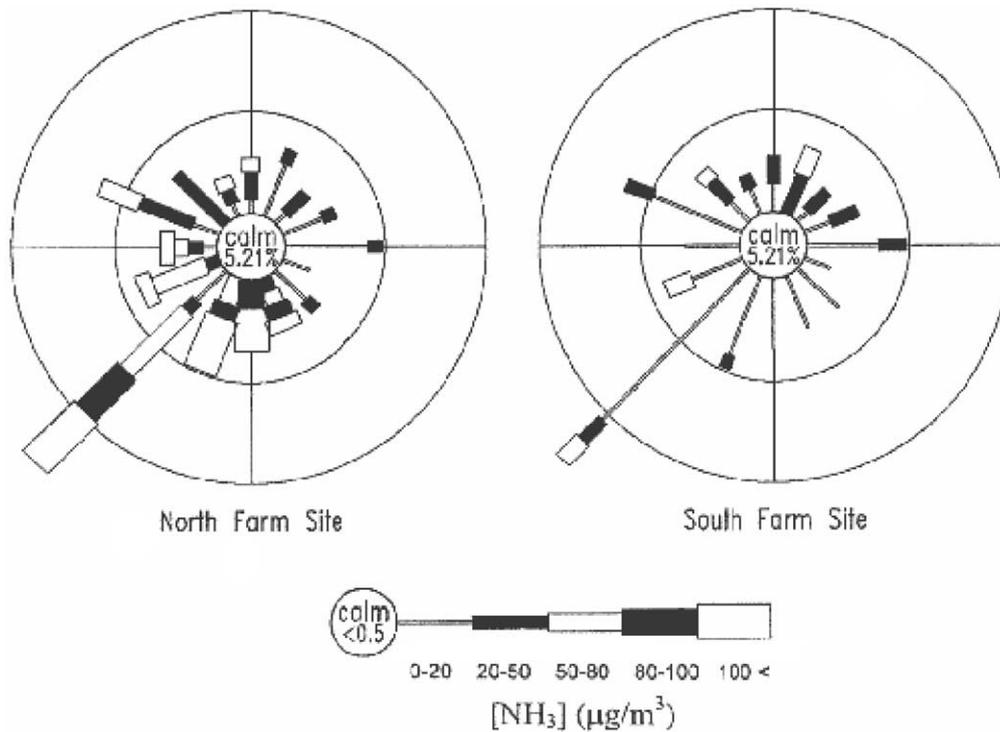


Fig. 2. Frequencies of ammonia concentration regime by wind direction.

Table 1

Equivalent molar ratios of $\text{NH}_4^+/\text{SO}_4^-$, $\text{NH}_4^+/\text{NO}_3^-$, and $\text{NH}_4^+/(\text{SO}_4^- + \text{NO}_3^- + \text{Cl}^-)$, and the percentage of aerosol constituents

Site	$\text{NH}_4^+/\text{SO}_4^-$	$\text{NH}_4^+/\text{NO}_3^-$	$\text{NH}_4^+/(\text{SO}_4^- + \text{NO}_3^- + \text{Cl}^-)$	NH_4^+ (%)	SO_4^- (%)	NO_3^- (%)	Cl^- (%)
North Farm	1.39	3.97	0.99	60.53	21.75	15.26	2.47
South Farm	1.32	3.61	0.93	59.09	22.30	16.37	2.24

deposition of material. However, considering the effects of dry deposition of ammonia gas on contribution of ammonia source to receptor, the partial reflecting assumption developed by Overcamp (1976) is used. The contribution of ammonia source to a receptor is reduced by a factor (α) called the reflection coefficient [Eq. (1b)]. When $\alpha=1$, the lower boundary can be described by the perfectly reflecting assumption, and the upper boundary by the non-reflecting assumption ($\alpha=0$). In this partial reflection model, the mean concentration is given by Eq. (1a) for steady-state condition, and the expression for the reflection coefficient at $z=0$ is given by Eq. (1b), where i is the number of cells which contribute to receptor ammonia concentration (McCulloch, 1999):

$$\bar{C}_i(x, y, z, t) = \frac{Q_{\text{NH}_3}}{2\pi\bar{u}\sigma_y\sigma_z} \exp\left(-\frac{y_i^2}{2\sigma_y^2}\right) \left\{ \exp\left[-\frac{(z-H)^2}{2\sigma_z^2}\right] + \alpha(x, z) \exp\left[-\frac{(z+H)^2}{2\sigma_z^2}\right] \right\} \quad (1a)$$

$$\alpha_o(x) = 1 - \frac{2v_d}{\left(v_d + \frac{\bar{u}H}{\sigma_z} \frac{d\sigma_z}{dx}\right)} \quad (1b)$$

\bar{C}_i is the average concentration at the downwind receptor of the source; \bar{u} is the effective wind speed called the transport speed of the plume; Q_{NH_3} is the emission source strength of ammonia; σ_y and σ_z are the lateral and vertical dispersion parameters, respectively. α is the reflection coefficient; x_i is along-wind distance from the source; y_i is the crosswind distance from the center line of the plume to the receptor; z is the height of the receptor; H is the height of the emission source, and v_d is the dry deposition of NH_3 . For this study, NH_3 dry deposition value for the natural meadow of approximately 16 mm/s was used from (Sutton et al., 1993).

The exhaust fans of the animal housing units, and the waste lagoon were treated as point sources. The swine lagoon is divided into 40 cells, acting as individual point sources, rather than a single area source (Fig. 1). This approach allows us for a consistent modeling approach for both source types and various fractions for accurate

estimation of NH_3 contributions from sources (i.e. lagoon and/or barns) based on the influence of various fractions of the lagoon, depending upon the wind direction and short transport distances involved. A Gaussian dispersion model for estimating concentrations downwind of an area source which is divided into discrete multi-point sources located at the centers of grid cells has been used earlier and validated by Turner (1964) and McCulloch (1999). For the data selection, wind direction dependent geometric parameters were computed for each point source (Fig. 1). The fixed parameters are the north to south (a) and east to west (b) distances from each point source to the receptor, the resultant distance (r_i), the mean direction from which the wind is coming (Θ), and associated angle (α_i), where i is the number of cells which contribute to receptor ammonia concentration. For selecting the point sources, which contributed to the ammonia concentration at the receptor site, the crosswind distance ($y_i = r_i \sin(|\Theta - \alpha_i|)$) is compared to the estimated plume half-width ($2.15 \sigma_y$) at the downwind distance from the center of the lagoon to the receptor SF site. When the crosswind distance (y_i) is less than the plume half-width ($2.15 \sigma_y$), the point source is considered to contribute as a point source to the SF receptor. Average ammonia contributions to the receptor for 12 h is expressed as

$$[\text{NH}_3]_{\text{Lagoon},i,t} = \sum_{i=1}^n \left(\sum_{i=1}^m [\text{NH}_3]_{i,t} \right) / n$$

where i is the number of cells and n is the number of time which contribute to receptor ammonia concentration. Thus, the sum of ammonia concentration for each contributed lagoon point source to the receptor was indicated as $[\text{NH}_3]_{\text{Lagoon}}$. The ammonia concentration at the NF site was indicated as the background concentration expressed as $[\text{NH}_3]_{\text{NF}}$. The ammonia input data, $[\text{NH}_3]_{\text{NF} + \text{Lagoon}}$, for estimating the reaction rate constants is defined as the sum of ammonia concentration from the background NF site ($[\text{NH}_3]_{\text{NF}}$) and the NH_3 contribution associated with the swine lagoon ($[\text{NH}_3]_{\text{Lagoon}}$). Fig. 3 shows the general distribution of $[\text{NH}_3]_{\text{Lagoon}}$, σ_y , and \bar{u} estimated by a Gaussian dispersion model. While σ_y is fairly evenly distributed, most of the observations tend to be clustered around lower values of the effective wind speed and concentration.

5. Reaction rate constant

Gas-to-particle conversion occurs by physical (i.e. size distribution) and/or chemical processes of ammonia with sulfuric acid, nitric acid, and hydrochloric acid in the atmosphere [Eqs. (2a)–(2c)]. The following gas (g), liquid (l) and solid (s) phase reactions summarize ammonium aerosol production (Finlayson-Pitts and Pitts, 1986):

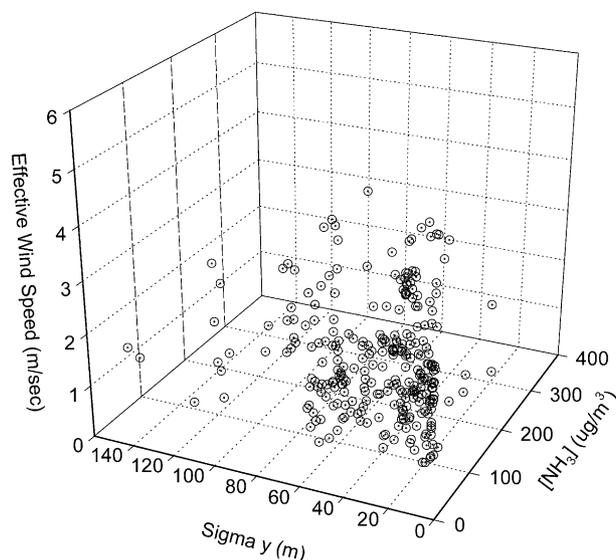
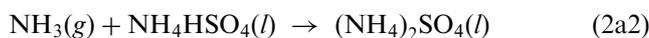


Fig. 3. Distributions of $[\text{NH}_3]_{\text{Lagoon}}$, σ_y and σ_z , lateral and vertical dispersion parameters, respectively.



Because this study site is dominated by ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$, the reaction rate between NH_3 and H_2SO_4 aerosol was estimated from Eq. (2a) [Eq. (3)].

$$\frac{d[\text{NH}_3]}{dt} = -2k_S \cdot [\text{NH}_3]^2 \quad (3)$$

Warneck (2000) suggested that the reaction between NH_3 and H_2SO_4 aerosol is preferred over reactions with HNO_3 and HCl . Therefore, in this study, we assumed that NH_3 reacts primarily with H_2SO_4 . Using the following boundary conditions, $\tau = 0$: $[\text{NH}_3]_0 = [\text{NH}_3]_{\text{NF} + \text{Lagoon}}$; $\tau = T$: $[\text{NH}_3]_T = [\text{NH}_3]_{\text{SF}}$, the following solution [Eq. (5)] to Eq. (4) is obtained.

$$[\text{NH}_3]_\tau = \frac{[\text{NH}_3]_0}{2k_S \cdot \tau \cdot [\text{NH}_3]_0 + 1} \quad (4)$$

where $[\text{NH}_3]_{\text{SF}}$ is the concentration of ammonia at receptor, i.e. SF site, and T is the total transport time

from source to receptors which is estimated by considering mean wind speed and transport distance between the NF and SF site. Thus, the rate constant (k_S) between NH_3 and H_2SO_4 aerosol is determined as:

$$k_S = \frac{1}{2} \times \frac{[\text{NH}_3]_{\text{NF+Lagoon}} - [\text{NH}_3]_{\text{SF}}}{[\text{NH}_3]_{\text{NF+Lagoon}} \times [\text{NH}_3]_{\text{SF}}} \times \frac{1}{T} \quad (5)$$

Similarly, the rate concentration of ammonia with nitric acid is derived by substituting Eq. (4) into Eq. (6a):

$$\frac{d[\text{HNO}_3]}{d\tau} = -k_N \cdot [\text{NH}_3]_{\tau} [\text{HNO}_3] \quad (6a)$$

$$\int_{[\text{HNO}_3]_0}^{[\text{HNO}_3]_{\tau}} \frac{1}{[\text{HNO}_3]} d[\text{HNO}_3] = -k_N \int_0^T [\text{NH}_3]_{\tau} d\tau \quad (6b)$$

$$\int_{[\text{HNO}_3]_0}^{[\text{HNO}_3]_{\tau}} \frac{1}{[\text{HNO}_3]} d[\text{HNO}_3] = -k_N \int_0^T \left(\frac{[\text{NH}_3]_{\text{NF+Lagoon}}}{2k_S \cdot t \cdot [\text{NH}_3]_{\text{NF+Lagoon}} + 1} \right) d\tau \quad (6c)$$

$$k_N = -k_S \cdot \ln \left[\frac{[\text{HNO}_3]_{\text{SF}}}{[\text{HNO}_3]_{\text{NF}}} \right] \times \frac{1}{\ln(2k_S \cdot T \cdot [\text{NH}_3]_{\text{NF+Lagoon}} + 1)} \quad (6d)$$

Similarly, the rate concentration of ammonia with hydrochloric acid is derived [Eq. (7)]:

$$k_{\text{Cl}} = -k_S \cdot \ln \left[\frac{[\text{HCl}]_{\text{SF}}}{[\text{HCl}]_{\text{NF}}} \right] \times \frac{1}{\ln(2k_S \cdot T \cdot [\text{NH}_3]_{\text{NF+Lagoon}} + 1)} \quad (7)$$

The first order rate constant between ammonia and sulfuric acid was estimated for comparison with other studies (Lenhard and Gravenhorst, 1980; Vermetten et al., 1985; Erisman et al., 1988; Harrison and Kitto, 1992). From Eq. (2a1) reaction, the first order rate constant, k_{S-1} , was defined:

$$\frac{d[\text{NH}_3]}{dt} = -k_{S-1} \cdot [\text{NH}_3] \quad (8a)$$

$$[\text{NH}_3]_{\tau} = [\text{NH}_3]_0 \times e^{k_{S-1} \cdot t} \quad (8b)$$

$$k_{S-1} = -\ln \left[\frac{[\text{NH}_3]_{\text{SF}}}{[\text{NH}_3]_{\text{NF+Lagoon}}} \right] \times \frac{1}{T} \quad (8c)$$

6. Results and discussion

6.1. Rate constants between acid gases and ammonia

This study has focused on separate neutralization process based on a combination of observational data. Data were segregated by wind direction in which air moved from the ammonia source, i.e. lagoon to the receptor. In only selected cases, the contribution of ammonia concentration at the SF site ($[\text{NH}_3]_{\text{NF+Lagoon}}$), $[\text{NH}_3]_{\text{SF}}$, and transport time are presented in Table 2. From the combined error 45.86% from a Coupled Mass Transfer and Chemical Equilibrium Reaction model (Aneja et al., 2001) and a Gaussian dispersion mode (McCulloch, 1999), the accuracy of the mean pseudo-first-order k_{S-1} between NH_3 and H_2SO_4 aerosol is approximately $\pm 81.28\%$ based on error propagation theory for the product of $[\text{NH}_3]$ contributions and transport time scale. Table 3 shows the rate constants between NH_3 , and acid gases at a commercial hog farm. The mean second order rate constants of NH_3 with H_2SO_4 , HNO_3 , and HCl are $k_S = 1.14 (\pm 1.25) \times 10^{-4} \text{ m}^3/\mu\text{mol/s}$, $k_N = 0.73 (\pm 1.49) \times 10^{-4} \text{ m}^3/\mu\text{mol/s}$, and $k_{\text{Cl}} = 0.86 (\pm 1.44) \times 10^{-4} \text{ m}^3/\mu\text{mol/s}$, respectively. The rate constants, k_S , between NH_3 and H_2SO_4 aerosol shows relatively greater than k_N and k_{Cl} presented here. However, determination of confidence in k_N and k_{Cl} estimations is questionable due to the complex reversible reactions, which are a function of temperature and RH arising error (Tang and Munelwitz, 1977; Tang, 1980; Stelson and Seinfeld, 1982a,b).

The mean pseudo-first-order k_{S-1} between NH_3 and H_2SO_4 aerosol is $5.00 (\pm 3.77) \times 10^{-3} \text{ s}^{-1}$, consistent with other study model results and experimental data derived by other methods (Huntzicker et al., 1980; McMurry et al., 1983; Erisman et al., 1988; Harrison and Kitto, 1992). Erisman et al. (1988) calculated an average conversion rate of $1 \times 10^{-4} \text{ s}^{-1}$ for daytime periods and $5 \times 10^{-5} \text{ s}^{-1}$ for nighttime periods from the vertical concentration distribution. Harrison and Kitto (1992) modified the rate constant from Erisman et al. (1988) by substituting ammonia and ammonium horizontal distribution, and indicated a pseudo-first-order rate constant for this reaction within the range $4 \times 10^{-6} \text{ s}^{-1}$ to $4.1 \times 10^{-4} \text{ s}^{-1}$. However, the uncertainty arises from large-scale distance between sites, and large sampling periods (24 h) from Harrison and Kitto (1992), and vertical inhomogeneity in the boundary layer from Erisman et al., (1988). Asman and Van Jaarsveld (1990) used a value of $8 \times 10^{-5} \text{ s}^{-1}$ in their long-range transport model for modeling of ammonia and ammonium in Europe. Vermetten et al. (1985) also suggested a value of a rate constant from 10^{-5} to 10^{-3} s^{-1} in the lowest 100 m. Lenhard and Gravenhorst (1980) who estimated the rate constant ($\approx 2.1 \times 10^{-5} \text{ s}^{-1}$) at 400 m heights suggested that greater values for conversion rate might

occur at lower elevation levels. Thus, the pseudo-first-order rate constant k_{S-1} presented here shows in agreement with other studies.

6.2. Effects of meteorological factors on rate constant

The rate constant is expected to be dependent on the concentrations of ammonia and acidic substances, temperature, relative humidity, and the mixing of the boundary layer (McMurray et al., 1983; Harrison and Kitto, 1992). Increasing relative humidity results in the growth of the liquid water content of particulate matter due to the increased absorbing capacity of aerosols with regard to gaseous sulfuric acid and nitric acid. Hence, particle size increases due to condensation of liquid water under high RH conditions. Huntzicker et al. (1980) and McMurray et al. (1983) suggested that the reaction rate between NH_3 with H_2SO_4 aerosol decreases with increasing particle size (i.e. higher RH). Thus, the extent of neutralization process could be affected by the particle size and the deliquescent and hygroscopic properties of aerosol products (Tang and Munkelwitz, 1977). Fig. 4 shows the relationship between k_{S-1} and ambient temperature, relative humidity, solar radiation, and wind speed in the atmosphere, respectively. The mean pseudo-first-order rate constant, k_{S-1} , displays positive relationships between the rate constant and

ambient temperature ($r=0.49$), solar radiation ($r=0.54$), and wind speed ($r=0.69$). However, relative humidity shows a negative correlation with the rate constant ($r=-0.68$), due to the decreasing of the reaction rate as the extent of reaction progressed by increasing relative humidity (Huntzicker et al., 1980; McMurray et al., 1983). On the other hand, wind speed has a positive correlation with the rate constant ($r=0.69$). The reason for this positive relationship could be due to the increasing ammonia emission associated with increasing wind speed (Aneja et al., 2001).

6.3. Determination of the NH_4NO_3 dissociation constant

The volatility of ammonium nitrate being higher than that of ammonium sulfate is dependent on the water content of the aerosol. The existing states between ammonium nitrate, and gaseous nitric acid and ammonia are affected by the amount of water in the atmosphere. Deliquescence of Relative Humidity (DRH) of NH_4NO_3 was determined by Tang and Munkelwitz (1977), and Tang (1980) as 62% RH. Under less than 62% RH, ammonium nitrate exists between both aerosol and gas phases. Therefore, the equilibrium relationship between NH_3 and HNO_3 in the gas phase and particulate NH_4NO_3 were examined, and compared with the theoretical equilibrium dissociation constant estimated by Stelson et al. (1979), and Kim et al. (1993a) based on the observed data. This equilibrium constant can then be applied under the assumption of immiscible pure particulate ammonium nitrate. For analysis of the relationship of $\text{NH}_3/\text{HNO}_3/\text{NH}_4\text{NO}_3$, the estimated theoretical equilibrium constant was used to compare the measured data in these ammonia rich sites (Fig. 5). The results indicate the aerosol composition consisted of pure ammonium nitrate or a mixed composition. Cadle et al. (1982) have shown that the theoretical products of $[\text{NH}_3][\text{HNO}_3]$ in urban sites and rural sites are related to the NH_4NO_3 equilibrium constant. In urban sites, theoretical products were shown to be close to the

Table 2
Mean $[\text{NH}_3]$ contribution to the receptor ($[\text{NH}_3]_{\text{NF+Lagoon}}$), $[\text{NH}_3]$ at the SF site ($[\text{NH}_3]_{\text{SF}}$), and transport time (T)

	$[\text{NH}_3]_{\text{NF+Lagoon}}$ ($\mu\text{g}/\text{m}^3$)	$[\text{NH}_3]_{\text{SF}}$ ($\mu\text{g}/\text{m}^3$)	Transport Time (s)
Mean	77.86	15.66	443.03
STD ^a	74.39	11.25	291.88
Maximum	166.32	58.39	1617.65
Minimum	13.94	2.88	161.29

^a STD = Standard Deviation.

Table 3
Mean values of reaction rate constants between ammonia and sulfuric acid, nitric acid, and hydrochloric acid

Time	k_{S-1} (s^{-1})	k_S ($\text{m}^3/\mu\text{mol}/\text{s}$)	k_N ($\text{m}^3/\mu\text{mol}/\text{s}$)	k_{Cl} ($\text{m}^3/\mu\text{mol}/\text{s}$)
Mean	5.00×10^{-3}	1.14×10^{-4}	7.30×10^{-5}	8.56×10^{-5}
STD ^a	$(\pm 3.77 \times 10^{-3})$	$(\pm 1.25 \times 10^{-4})$	$(\pm 1.49 \times 10^{-4})$	$(\pm 1.44 \times 10^{-4})$
DF ^b	51	51	18	31
Daytime	5.94×10^{-3}	1.19×10^{-4}	4.44×10^{-5}	8.53×10^{-5}
STD	$(\pm 3.73 \times 10^{-3})$	$(\pm 9.93 \times 10^{-5})$	$(\pm 3.09 \times 10^{-5})$	$(\pm 7.44 \times 10^{-5})$
DF	24	24	11	14
Nighttime	3.79×10^{-3}	9.94×10^{-5}	1.18×10^{-4}	8.58×10^{-5}
STD	$(\pm 3.51 \times 10^{-3})$	$(\pm 1.45 \times 10^{-4})$	$(\pm 2.40 \times 10^{-4})$	$(\pm 1.82 \times 10^{-4})$
DF	27	27	7	17

^a STD = Standard Deviation.

^b DF = Degree of Freedom

equilibrium constant and, in rural sites, some of data were shown to be both above and below the equilibrium constant. The factors leading to these differences between each site were determined as being topographical and meteorological. Harrison and Misibi (1994) applied this concept to suburban sites, and

showed rather close agreement with the theoretical prediction of the concentration product based on equilibrium chemical thermodynamics. In this ammonia-rich environment, the observed $[\text{NH}_3][\text{HNO}_3]$ products are above the predicted equilibrium constant for NH_4NO_3 . The lack of RH influence on the

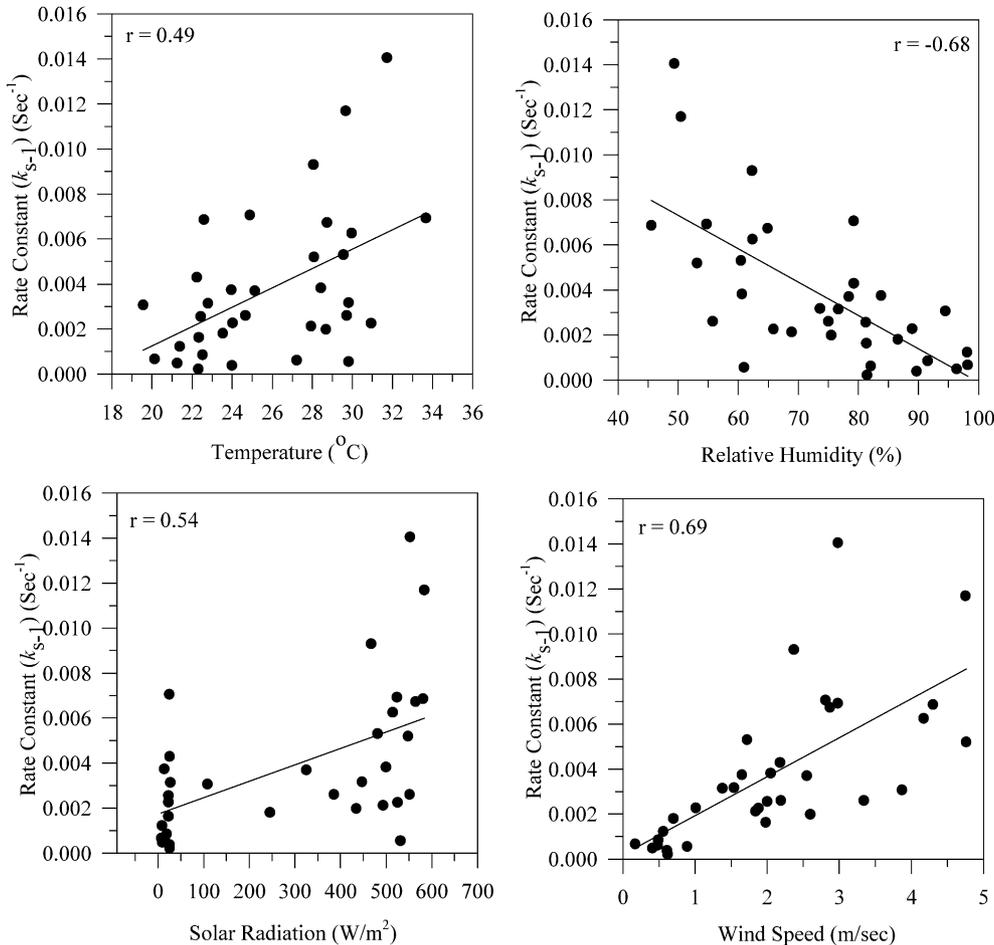


Fig. 4. Relationship of reaction rate constant (k_{s-1}) between NH_3 and H_2SO_4 aerosol with meteorological factors.

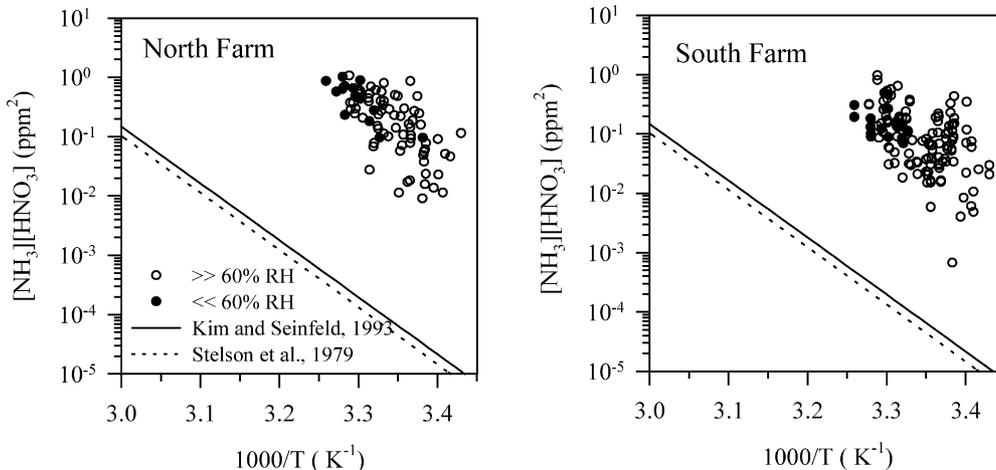


Fig. 5. The comparison of the measured concentration products of $[\text{NH}_3][\text{HNO}_3]$ with the theoretical equilibrium constants at the NF and SF sites!

$[\text{NH}_3][\text{HNO}_3]$ products indicate that local sources of NH_3 are present. Therefore, due to the local excess of ammonia, this location (at a hog farm) has different characteristics of the observed $[\text{NH}_3][\text{HNO}_3]$ products than the theoretical equilibrium constant of ammonium nitrate.

7. Conclusion

The rate constant of ammonia with acidic gases was estimated based on two sampling sites, i.e. a background and a receptor site, at a commercial hog farm in eastern North Carolina. The rate constants of ammonia with sulfuric acid, nitric acid and hydrochloric acid are $k_S = 1.14 (\pm 1.25) \times 10^{-4} \text{ m}^3/\mu\text{mol/s}$, $k_N = 0.73 (\pm 1.49) \times 10^{-4} \text{ m}^3/\mu\text{mol/s}$, and $k_{\text{Cl}} = 0.86 (\pm 1.44) \times 10^{-4} \text{ m}^3/\mu\text{mol/s}$. The pseudo-first-order k_{S-1} estimation approximated $\sim 5.00 (\pm 3.77) \times 10^{-3} \text{ s}^{-1}$ is in good agreement with other studies (Lenhard and Gravenhorst, 1980; Vermetten et al., 1985). From analysis of the relationship of the mean pseudo-first-order rate constant (k_{S-1}) with meteorological factors, this rate constant is positively correlated with temperature, solar radiation, and wind speed. However, relative humidity has a negative correlation with the pseudo-first rate constant, as the result of decreasing the reaction rate by the extent of neutralization reactions of ammonia in the atmosphere. This observational based approach coupled with dispersion model provides a useful methodology for estimating the rate constants directly in the atmosphere.

The equilibrium dissociation constant analysis was used as an effective method to determine the characteristics of aerosols in an ammonia rich rural environment. The observed $[\text{NH}_3][\text{HNO}_3]$ products exceeded values predicted by theoretical equilibrium constants, due to a local excess of ammonia concentration.

The study of the portioning of NH_3 between gas and around phase is important for the prediction of long-range transport of acidifying and eutrophying air pollutants, air quality, and climate change. This measurement and analysis provides data from a little studied part of US (i.e., agricultural/rural Southeast US) whose pollutions climate is distinctly different from the rest of the country due to strong local sources of ammonia i.e. intensively managed animal and crop agriculture.

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