

Measurement and Analysis of the Relationship between Ammonia, Acid Gases, and Fine Particles in Eastern North Carolina

Bok Haeng Baek and Viney P. Aneja

Department of Marine, Earth, and Atmospheric Sciences, North Carolina State University, Raleigh, North Carolina

ABSTRACT

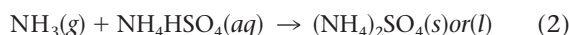
An annular denuder system, which consisted of a cyclone separator; two diffusion denuders coated with sodium carbonate and citric acid, respectively; and a filter pack consisting of Teflon and nylon filters in series, was used to measure acid gases, ammonia (NH₃), and fine particles in the atmosphere from April 1998 to March 1999 in eastern North Carolina (i.e., an NH₃-rich environment). The sodium carbonate denuders yielded average acid gas concentrations of 0.23 μg/m³ hydrochloric acid (standard deviation [SD] ± 0.2 μg/m³); 1.14 μg/m³ nitric acid (SD ± 0.81 μg/m³), and 1.61 μg/m³ sulfuric acid (SD ± 1.58 μg/m³). The citric acid denuders yielded an average concentration of 17.89 μg/m³ NH₃ (SD ± 15.03 μg/m³). The filters yielded average fine aerosol concentrations of 1.64 μg/m³ ammonium (NH₄⁺; SD ± 1.26 μg/m³); 0.26 μg/m³ chloride (SD ± 0.69 μg/m³), 1.92 μg/m³ nitrate (SD ± 1.09 μg/m³), and 3.18 μg/m³ sulfate (SO₄²⁻; SD ± 3.12 μg/m³). From seasonal variation, the measured particulates (NH₄⁺, SO₄²⁻, and nitrate) showed larger peak concentrations during summer, suggesting that the gas-to-particle conversion was efficient during summer. The aerosol fraction in this study area indicated the domination of ammonium sulfate particles because of the local abundance of NH₃, and the long-range transport of SO₄²⁻ based on back trajectory analysis. Relative humidity effects on gas-to-particle conversion processes were analyzed by

particulate NH₄⁺ concentration originally formed from the neutralization processes with the secondary pollutants in the atmosphere.

INTRODUCTION

Atmospheric acid gases (sulfuric acid [H₂SO₄], nitric acid [HNO₃], and hydrochloric acid [HCl]) have not only been identified as major contributors to the acidification of soils and precipitation but are also associated with adverse health effects, mainly respiratory diseases.¹ H₂SO₄ and HNO₃, the major acidic gases in the atmosphere, come from oxidation of sulfur dioxide (SO₂) to H₂SO₄ and oxides of nitrogen (NO_x) to HNO₃, respectively. These acid gases are neutralized in the atmosphere by ammonia (NH₃), the principal gaseous alkaline species. Thus, this neutralizing agent not only plays a role in determining acidification and eutrophication of ecosystems but also neutralizes acidic species in the atmosphere. Further, through gas-to-particle conversion processes, the acid gases and NH₃ are involved in fine particulate matter formation (PM_{fine} ≤ 2.5 μm).^{2–4}

Gas-to-particle conversion can be accomplished by condensation, which adds mass onto pre-existing aerosols, or by direct nucleation from gaseous precursors, forming an aerosol. Gas-to-particle conversion strongly depends on the concentration of acid gases and water vapor in the atmosphere.^{5–7} NH₃ reacts with H₂SO₄, HNO₃, and HCl; gases to form aerosols⁶ such as ammonium sulfate ((NH₄)₂SO₄), ammonium bisulfate (NH₄HSO₄), ammonium nitrate (NH₄NO₃), and ammonium chloride (NH₄Cl). Ammonium (NH₄⁺) salts formed by these reactions can exist as solid particles or liquid droplets depending on the amount of water vapor in the atmosphere. NH₃ preferentially reacts with H₂SO₄ to form NH₄HSO₄ and (NH₄)₂SO₄ through eqs 1 and 2.



IMPLICATIONS

This study provides a fundamental understanding of gas-to-particle conversion processes in an NH₃-rich environment, especially as agriculture air quality-related issues are becoming of importance at the national and international levels. This paper provides data and an observational-based analysis from a little studied part of the United States (i.e., rural and agricultural) whose pollution climate is distinctly different from the rest of the country because of the presence of strong local sources of NH₃ (i.e., intensively managed animal and crop agriculture).

NH_3 also can undergo an equilibrium reaction with gas-phase HNO_3 in the atmosphere to form NH_4NO_3 as shown in eq 3.



The low vapor pressure of H_2SO_4 allows it to condense easily on particle and droplet surfaces. Because the rate of condensation is dependent on the amount of water vapor in the atmosphere, H_2SO_4 is seldom found in the gas phase. However, HNO_3 is much more volatile than H_2SO_4 and not likely to form particles by homogeneous or heterogeneous nucleation. Therefore, because of its volatility, particulate NO_3^- is believed to be lower in concentration than SO_4^{2-} .⁶⁻⁹ However, particulate NO_3^- can be the dominant species in PM_{fine} when in SO_4^{2-} -limited regimes.

In general, NH_3 , HNO_3 , and H_2SO_4 are highly soluble inorganic species in the atmosphere, and they are efficiently removed by wet/dry deposition or rain out and by neutralization processes. Increasing relative humidity (RH) results in an increase of the growth in the liquid water content of PM, thereby increasing the absorbing capacity of aerosol with regard to gaseous H_2SO_4 and HNO_3 . NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ are effective condensation nuclei,¹ facilitating droplet formation. As a result of these mechanisms, the composition of aerosols in a local area is largely influenced by the concentration of NH_3 , H_2SO_4 , HNO_3 , and water vapor in the atmosphere.^{10,11} Thus, gas-to-particle conversion processes can determine the lifetime of NH_3 and NH_4^+ , where NH_x ($\text{NH}_3 + \text{NH}_4^+$), in the atmosphere. The spatial scale of NH_3 as a contributor to total atmospheric nitrogen (N) deposition is governed in part by the gas-to-particle conversion rate of NH_3 to NH_4^+ . NH_3 has a short lifetime, ~ 0.5 – 5 days or less,¹²⁻¹⁴ because of the rapid gas-to-particle conversion of NH_3 to NH_4^+ and relatively high dry deposition velocity to the surfaces near its source. The NH_3 , which is not deposited or scavenged by rain, will undergo conversion to particulate NH_4^+ . NH_4^+ , which has a longer lifetime, ~ 5 – 10 days,¹⁴ will be transported longer distances downwind from its sources. Thus, if NH_3 deposits near its source, less NH_4^+ will be made available for long-range transport. For a more complete understanding of atmospheric NH_3 , it is necessary to differentiate between gaseous NH_3 and particulate NH_4^+ .

Interest in atmospheric NH_3 has increased over the past several years because of its role as a source of fixed N to soil and plants. On a global scale, domestic animals have been shown to be the largest source of NH_3 .^{1,12-15} In North Carolina, swine operation sources during 1996 contributed $\sim 21\%$ of total N emissions from combined NO_x and NH_3 sources (~ 3 Tg-N/yr), and NH_3 emissions from swine are $\sim 48\%$ ($\sim 68,450$ t NH_3 -N/yr) of the total NH_3

emission.¹⁴ Thus, swine operation is one of the most significant NH_3 emission sources in North Carolina.¹²⁻¹⁴ Eastern North Carolina, which has a high population density of domestic livestock in North Carolina, has been characterized as being NH_3 -rich and having corresponding NH_4^+ aerosols, which are dominated by sulfates.¹⁶ Current regulations under the Clean Air Act (CAA) directed toward surface O_3 control are likely to reduce NO_x emissions, while emissions of NH_3 could grow further in the future. These evolving emission scenarios potentially could have significant impact on troposphere chemical composition over North America.

In this study, the concentrations of NH_3 , acid gases, and aerosol species have been measured by an annular denuder system (ADS)¹⁷ at a commercial hog farm in eastern North Carolina during April 1998–March 1999. The measured data were not only used for analyzing the general characteristics of NH_3 , H_2SO_4 , and HNO_3 , but also to examine the gas-to-particle conversion between NH_3 and acid gases. The mass concentrations of PM_{fine} at this intensively managed animal agricultural site were compared and contrasted with several (urban, rural, remote, and marine) locations through case studies, due to the fact that condensation of HNO_3 and H_2SO_4 is largely dependent on RH in the atmosphere. Thus, effects of RH on conversion rate also were analyzed. Lastly, the origin of the air masses (based on back trajectory analysis) also was studied.

MEASUREMENTS

The study area consisted of two measurement sites at a commercial hog farm in eastern North Carolina, dubbed North Farm (NF) site and South Farm (SF) site. The NF site was located ~ 50 m northeast of the swine waste storage and treatment lagoon, and the SF site was located ~ 400 m south-southwest of the waste lagoon. Samples were collected using the ADS from April to July 1998 at the NF site and from April 1998 to March 1999 at the SF site. The ADS system consists of three major parts: a cyclone separator, which removes coarse particles greater than 2.5 μm aerodynamic diameter and thereby prevents neutralization of acid gases; two diffusion denuders in series, coated with sodium carbonate (NaCO_3) and citric acid for collecting NH_3 and acid gases, respectively; and finally, a filter pack containing a Teflon and a nylon filter in series, which collects fine particles¹⁷ (see Figure 1). The sampler inlets were ~ 4 m above the ground. Sampling flow rates and intervals were controlled using mass flow controllers and electronic timers, respectively. The samplers were operated at a constant flow rate of 10 L/min. ADS measurements were derived from 12-hr integrated samples, representing daytime (7:00 a.m.–6:00 p.m.) and nighttime averages (7:00 p.m.–6:00 a.m.).

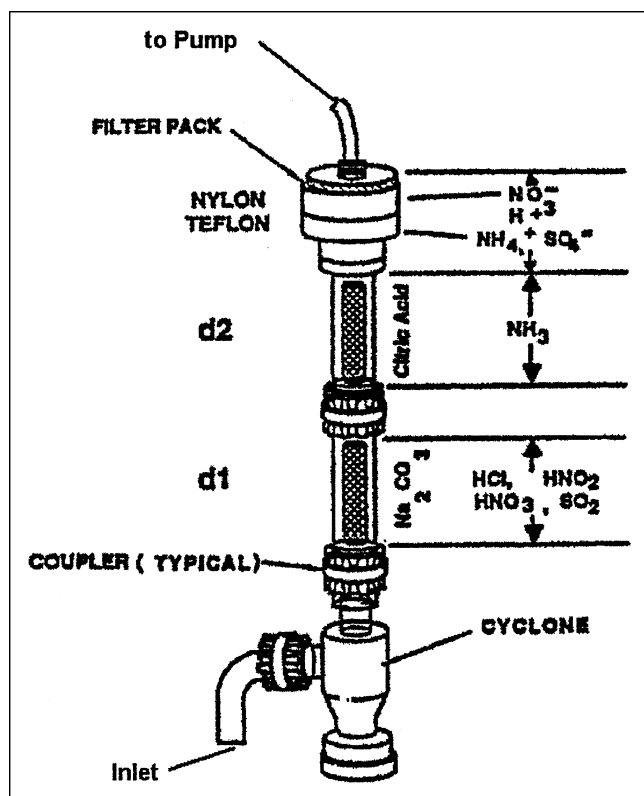


Figure 1. ADS.

The NaCO_3 denuders coated with 1% glycerine and 1% NaCO_3 in a 50% mixture of methanol and distilled water collects average gas concentrations of HCl, nitrous acid (HONO), HNO_3 , and SO_2 . The citric acid denuders were coated with 2% citric acid in a 50% mixture of methanol and distilled water to capture NH_3 . The filter packs contained both 47-mm diameter membrane Teflon and nylon filters. The 2.0- μm pore size Teflon filter was used for fine particles containing NH_4^+ , chloride (Cl^-), NO_3^- , and SO_4^{2-} ions in the atmosphere. The 1.0- μm pore size nylon filter next to the Teflon filter was installed to capture NO_3^- from the NH_4NO_3 , which may have dissociated from the Teflon filter.

The denuder samples were extracted with deionized water, and the Teflon filters were extracted in a heated sonic bath with 10^{-4} N perchloric acid in a 2% mixture of methanol and deionized water. The nylon filters were extracted in a heated sonic bath. The extracted samples were analyzed for Cl^- , nitrite (NO_2^-), NO_3^- , and SO_4^{2-} by ion chromatography and for NH_4^+ by colorimetric flow injection analysis. A full description of this methodology can be found in ref 18.

Meteorological parameters, including wind direction (WD), wind speed (WS), and ambient temperature (T), were measured at a tower near the SF site at 2- and 10-m elevation. RH was measured at 2 m. Solar radiation (SR) and precipitation were measured at ground level. All instrumental sensors were obtained from Campbell

Scientific, Inc., such as model 03001 Wind sentry Wind set to measure wind speed and wind direction; ASPTC aspirated shield with fine wire thermocouple model CS500 for measuring temperature and RH; model LI200X silicon pyranometer to measure color radiation; and model CS700-L to measure precipitation.

RESULTS AND DISCUSSION

Seasonal Variation

The SF measurements were used for seasonal variation analysis from April 1998 to March 1999 (see Figure 2). Data from the NF site were not used for seasonal variation analysis because measurements were only made from April to June 1998. Gaseous NH_3 and HNO_3 concentrations showed higher concentration during spring and summer. SO_2 had peak values during the winter, which can be attributed to (1) increased fuel usage during these months; and (2) reduced conversion of SO_2 to SO_4^{2-} . During summer, measured formations of the precursor secondary pollutants enhanced chemical reactions with NH_3 under higher RH, which increases the absorbing capacity of the aerosol with regard to gaseous HNO_3 and H_2SO_4 . Thus, the large peak of measured particulates (NH_4^+ , SO_4^{2-} , and NO_3^-) during summer suggests that gas-to-particle conversion is more efficient.

Gas-to-particle conversion in the atmosphere involves complex aqueous and gaseous chemical reactions.¹⁹ Table 1 lists the seasonal molar ratios of the measured concentrations. The molar ratio of $\text{SO}_4^{2-}/(\text{SO}_2 + \text{SO}_4^{2-})$, called the S ratio, is defined as the ratio of particulate SO_4^{2-} to total sulfur (S; $\text{SO}_2 + \text{SO}_4^{2-}$). The ratio is used as an indicator of air mass age, chemical conversion efficiency, and deposition. Also, the ratio of $\text{NO}_3^-/(\text{HNO}_3 + \text{NO}_3^-)$, which is the ratio of NO_3^- to total NO_3^- concentration, also called the N ratio, was used. A smaller ratio means a less efficient gas-to-particle conversion or a less efficient depletion of HNO_3 by dry deposition to the ground. Table 1 shows high $\text{SO}_4^{2-}/(\text{SO}_2 + \text{SO}_4^{2-})$ ratio during spring and summer, indicating that gas-to-particle conversion is occurring with the greatest efficiency during the warmer seasons in eastern North Carolina. The N ratio is highest in spring, while the summer value is similar to fall and winter values.

The relationships between particulates and NH_4^+ were analyzed. Figures 3 and 4 show the charge balance of NH_4^+ with SO_4^{2-} , NO_3^- , and the sum of acidic anion equivalent concentrations from April 1998 to March 1999. Each particulate species has a good correlation with NH_4^+ (SO_4^{2-} versus NH_4^+ , $R^2 = 0.624$ [$p < 0.05$], and NO_3^- versus NH_4^+ , $R^2 = 0.598$ [$p < 0.05$]; see Figure 3). A linear regression of the sum of particulate species against NH_4^+ improved the correlation ($R^2 = 0.808$; $p < 0.05$; see Figure 4). In Figure 3, they showed some differences

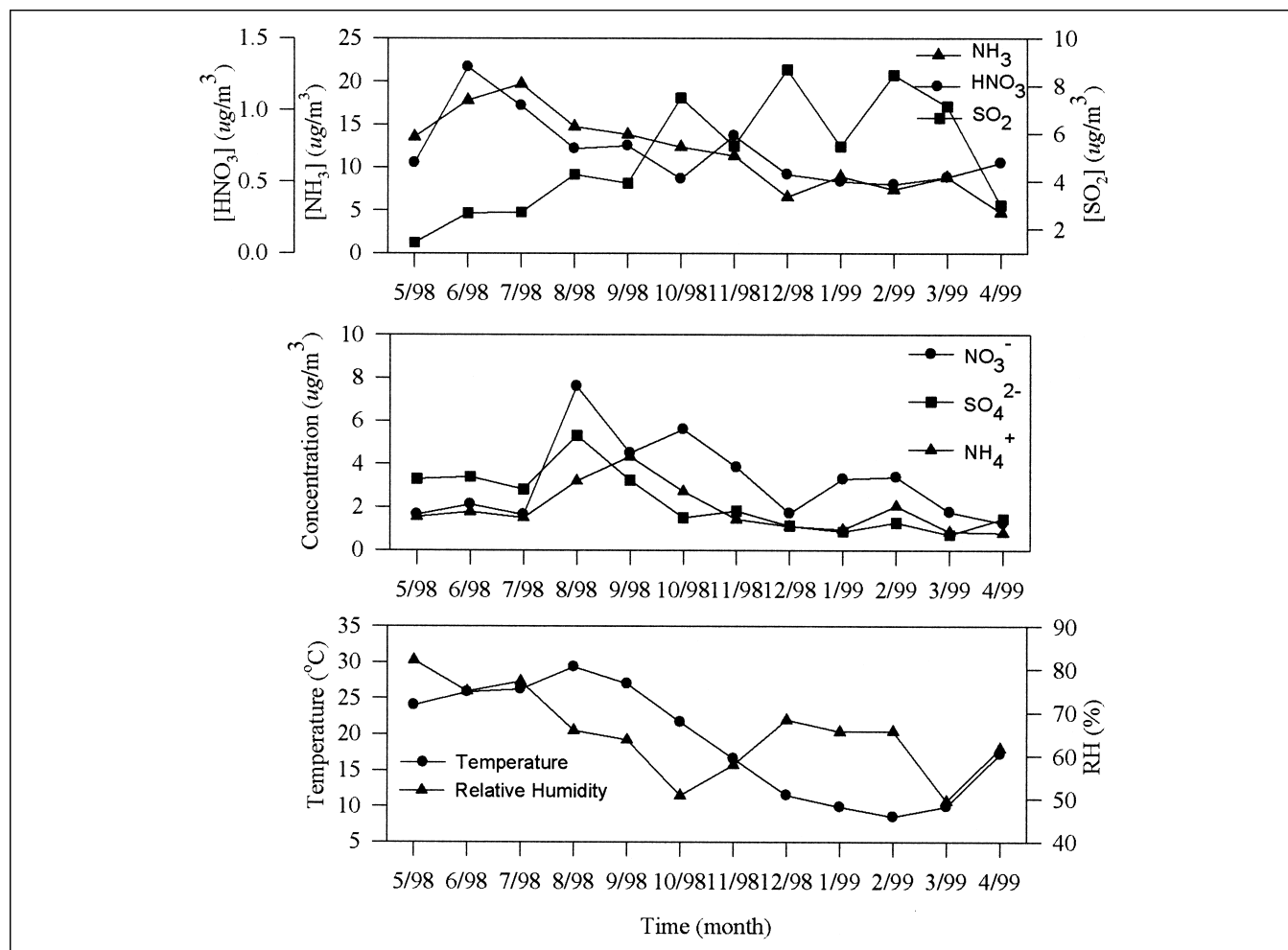


Figure 2. Seasonal variations of acidic gases, particulates, RH, and ambient temperature from April 1998 to March 1999 at the SF site.

between $[\text{SO}_4^{2-}]$ and $[\text{NO}_3^-]$ in aerosol composition, such as the high $[\text{SO}_4^{2-}]$ and low $[\text{NO}_3^-]$ called Case I (p), and low $[\text{SO}_4^{2-}]$ and high $[\text{NO}_3^-]$ called Case II (o). In Figure 4, when they are added together for comparing with NH_4^+ concentrations in aerosol composition, these special cases did not diminish the regression between NH_4^+ and sum of acidic anions but rather improved it between them. Thus, the case studies are provided in the next section.

Case Studies

Pacyna and Benson⁸ showed that sources of aerosols were characterized by the concentrations of SO_4^{2-} and NO_3^-

Table 1. Seasonal trends of ratios of $\text{SO}_4^{2-}/(\text{SO}_2 + \text{SO}_4^{2-})$ and $\text{NO}_3^-/(\text{HNO}_3 + \text{NO}_3^-)$, April 1998–March 1999, at the SF site.

Season	$\text{SO}_4^{2-}/(\text{SO}_2 + \text{SO}_4^{2-})$	$\text{NO}_3^-/(\text{HNO}_3 + \text{NO}_3^-)$
Spring	0.32	0.32
Summer	0.48	0.21
Fall	0.18	0.23
Winter	0.12	0.2

in the aerosols. Walker et al.²⁰ analyzed the spatial distribution of NH_4^+ and acidic particulates using a source-receptor regression model. Transport time or stagnation of an air mass over source regions can affect the chemical composition of aerosols. The type of the source region the air masses pass over is also crucial (e.g., agricultural versus industrial versus maritime). Therefore, in this study, backward trajectory analyses of air masses were conducted to provide indications of the source areas and the transport routes. In Figures 3 and 4, two cases have been identified that have relationships between SO_4^{2-} and NO_3^- in the aerosol composition. Case I (8/12/98, 8/29/98, and 9/28/98) was chosen as the dates that have high SO_4^{2-} and low NO_3^- , and Case II (8/21/98, 8/25/98, and 8/27/98) was chosen as the dates that have low SO_4^{2-} and high NO_3^- .

Table 2 lists average NH_3 , acid gases, and particulate concentrations for each case. Figure 5 provides 48-hr backward trajectory analysis at 500, 850, and 1000 mb at 18 UTC (14 EST) for Cases I and II. All dates in Case I having the high SO_4^{2-} and low NO_3^- concentration have been identified as having continental air masses, which are typically characterized by higher SO_2 concentrations.

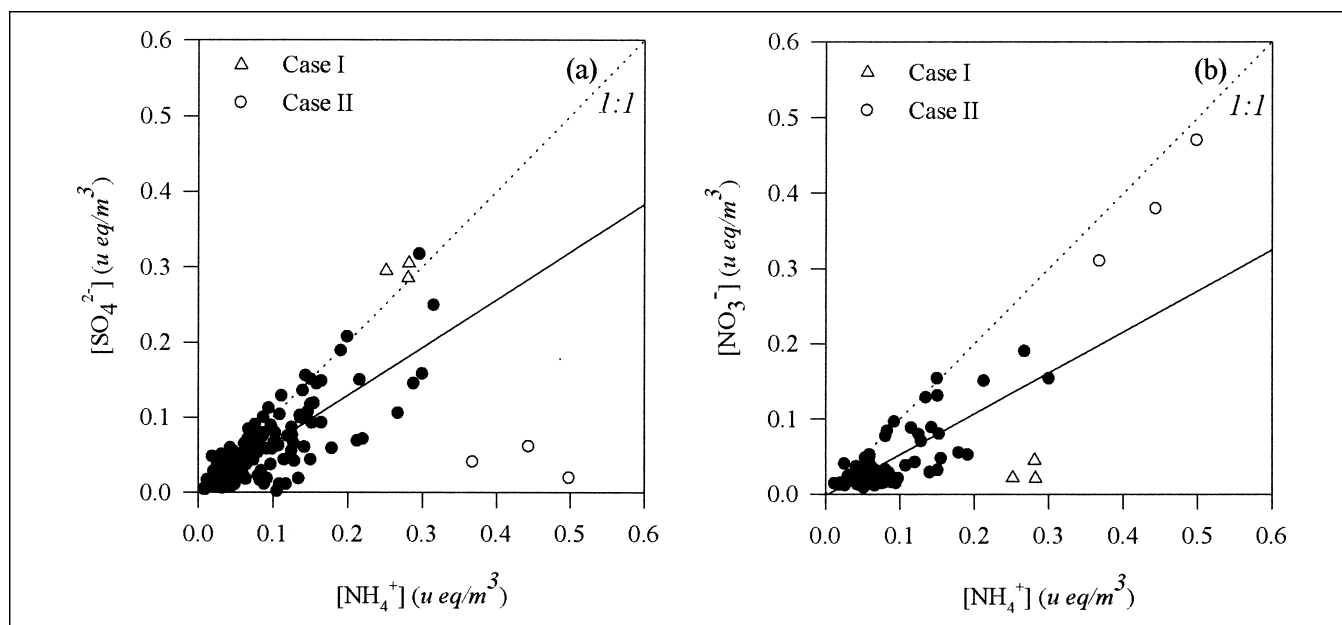


Figure 3. Charge balance between particulate ion and NH_4^+ equivalent concentrations from April 1998 to March 1999 at the SF site: (a) $[\text{NH}_4^+]$ vs. $[\text{SO}_4^{2-}]$. (b) $[\text{NH}_4^+]$ vs. $[\text{NO}_3^-]$.

In Case II, low SO_4^{2-} and high NO_3^- concentrations, the air masses pass over local biogenic NO_x -emitting areas and the high Cl^- concentration of marine areas. Thus, aerosol composition in Case II may be affected by local high NO_3^- concentration and marine high Cl^- concentration. However, aerosols in continental air mass might have characteristics with higher SO_2 and SO_4^{2-} concentration (high S ratio) because of the transport distance of continental air mass over source regions of high SO_2 emissions.

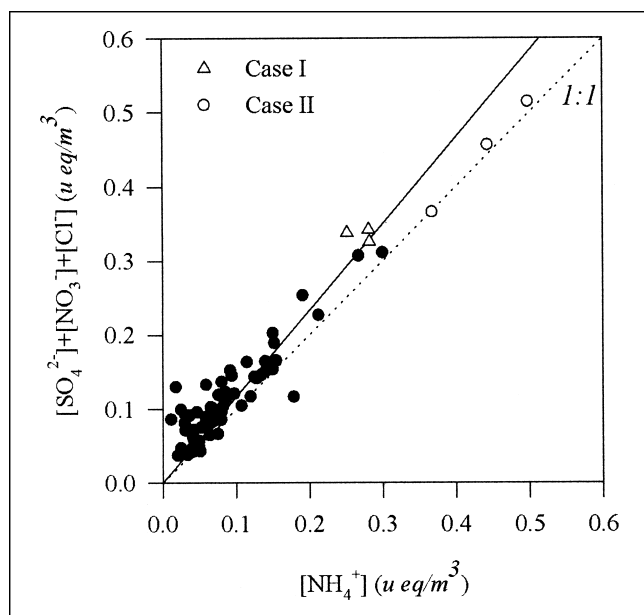


Figure 4. Charge balance between sum of SO_4^{2-} , NO_3^- , and Cl^- and NH_4^+ equivalent concentrations from April 1998 to March 1999 at the SF site.

COMPARISON OF NF AND SF

Table 3 shows the mass concentrations ($\mu\text{g}/\text{m}^3$) of air pollutants observed from April to July 1998 at both sites. Mean and standard deviation of NH_3 concentrations at the NF site ($54.54 \pm 39.82 \mu\text{g}/\text{m}^3$) showed much higher concentrations than that at the SF site ($17.89 \pm 15.03 \mu\text{g}/\text{m}^3$) because of its proximity to the swine lagoon by weak mean wind speed (0.36 m/sec) and 122° of dominant wind direction. Even though the dominant wind direction is not directly coming from the SF site located ~ 400 m south-southwest of the waste lagoon, weak winds could be a major factor for this difference. Mean concentrations of acidic gases, HNO_3 , H_2SO_4 , and HCl were $1.06 (\pm 0.84 \mu\text{g}/\text{m}^3)$, $3.23 (\pm 2.77 \mu\text{g}/\text{m}^3)$, and $0.77 (\pm 1.11 \mu\text{g}/\text{m}^3)$, respectively, at the NF site, and $1.14 (\pm 0.81 \mu\text{g}/\text{m}^3)$,

Table 2. Chemical analysis of case studies: mean concentration ($\mu\text{g}/\text{m}^3$) of NH_3 , acid gases, and PM_{fine} .

Date	NH_3 (g)	SO_2 (g)	HNO_3 (g)	HCl (g)	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-
Aug 12, 1998	18.04	11.22	1.65	1.01	5.07	14.64	1.29	0
Case I ^a								
Aug 29, 1998	7.68	2.83	0	0	3.45	14.17	1.34	0.75
Sept 28, 1998	8.91	1.95	0	0.27	5.05	13.7	2.79	0.41
Aug 21, 1998	4.57	2.56	0	1.74	6.64	1.94	19.2	0.54
Case II ^b								
Aug 25, 1998	26.66	1.56	0	1.57	8.99	0.91	29.13	0.88
Aug 27, 1998	8.93	0.03	0	1.61	7.99	2.93	23.51	0.54

^aCase I: Air masses with PM_{fine} having high SO_4^{2-} and low NO_3^- (i.e., continental air masses); ^bCase II: Air masses with PM_{fine} having low SO_4^{2-} and high NO_3^- concentration (i.e., air masses pass over local biogenic NO_x -emitting areas and high Cl^- concentration of marine areas).

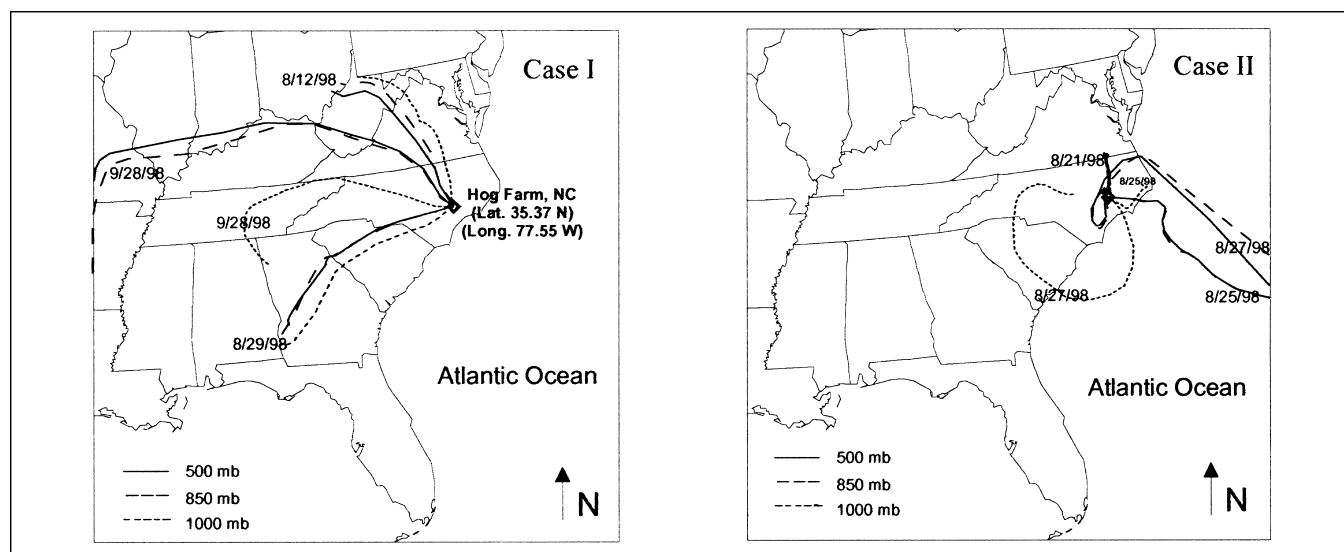


Figure 5. 48-hr backward trajectory analysis at 500, 850, and 1000 mb at 18 UTC (14 EST) at a hog farm located in eastern North Carolina on Case I (8/12/98, 8/28/98, and 9/28/98) and Case II (8/21/98, 8/25/98, and 8/27/98).

Table 3. Mass concentration ($\mu\text{g}/\text{m}^3$) of air pollutants observed, April–July 1998.

Species	Time	NF Mean ($\pm\text{SD}$) ^a	SF Mean ($\pm\text{SD}$) ^a
Gas			
NH ₃	all	54.54 (± 39.82)	17.89 (± 15.03)
	day	51.75 (± 33.82)	19.55 (± 15.57)
	night	57.23 (± 44.99)	16.1 (± 14.3)
HNO ₃	all	1.06 (± 0.84)	1.14 (± 0.81)
	day	1.53 (± 0.89)	1.48 (± 0.91)
	night	0.57 (± 0.37)	0.79 (± 0.51)
H ₂ SO ₄	all	3.23 (± 2.77)	1.61 (± 1.58)
	day	4.53 (± 3.06)	2.37 (± 1.75)
	night	1.91 (± 1.64)	0.81 (± 0.8)
HCl	all	0.77 (± 1.11)	0.23 (± 0.2)
	day	1.12 (± 1.34)	0.3 (± 0.23)
	night	0.42 (± 0.67)	0.15 (± 0.11)
Particulate			
NH ₄ ⁺	all	1.69 (± 1.27)	1.64 (± 1.26)
	day	1.62 (± 1.05)	1.76 (± 1.25)
	night	1.75 (± 1.46)	1.52 (± 1.27)
NO ₃ ⁻	all	1.63 (± 1.03)	1.92 (± 1.09)
	day	1.52 (± 0.93)	1.95 (± 1.34)
	night	1.71 (± 1.1)	1.9 (± 0.91)
SO ₄ ²⁻	all	3.11 (± 2.94)	3.18 (± 3.12)
	day	2.96 (± 2.47)	3.66 (± 3.31)
	night	3.27 (± 3.35)	2.66 (± 2.82)
Cl ⁻	all	0.22 (± 0.2)	0.26 (± 0.69)
	day	0.2 (± 0.22)	0.33 (± 1)
	night	0.24 (± 0.17)	0.2 (± 0.2)

^a ± 1 standard deviation.

1.61 ($\pm 1.58 \mu\text{g}/\text{m}^3$), and 0.23 ($\pm 0.11 \mu\text{g}/\text{m}^3$) at the SF site. The mean particulate NH₄⁺, SO₄²⁻, NO₃⁻, and Cl⁻ were 1.69 ($\pm 1.27 \mu\text{g}/\text{m}^3$), 3.11 ($\pm 2.94 \mu\text{g}/\text{m}^3$), 1.63 ($\pm 1.03 \mu\text{g}/\text{m}^3$), and 0.22 ($\pm 0.2 \mu\text{g}/\text{m}^3$), respectively, at the NF site, and 1.64 ($\pm 1.26 \mu\text{g}/\text{m}^3$), 3.18 ($\pm 3.12 \mu\text{g}/\text{m}^3$), 1.92 ($\pm 1.09 \mu\text{g}/\text{m}^3$), and 0.26 ($\pm 0.9 \mu\text{g}/\text{m}^3$) at the SF site.

HNO₃ had maximum concentrations during the daytime and minimum concentrations at night. Particulate NO₃⁻ shows the opposite trend, with higher concentrations during the night and lower during the day. The reason is that the diurnal variation of HNO₃ is anti-correlated with the decline in temperature. Connected with the nocturnal rise in RH is a growth in the liquid water content of PM, which increases the absorbing capacity of aerosols with regard to gaseous HNO₃ and H₂SO₄. Thus, SO₂ and SO₄²⁻ displayed similar temporal behavior to that of HNO₃ and NO₃⁻ over the continents. This may be explained by the negative correlation between HNO₃ and SO₂ diurnal cycles and RH.¹

The primary source of atmospheric NH₄⁺ is the gas-to-particle conversion processes of gaseous NH₃, neutralizing the acid gases (H₂SO₄, HNO₃) produced by the oxidation of SO₂ and NO₂, respectively. Thus, diurnal variation of NH₄⁺ concentrations depends largely on the concentration trends of H₂SO₄ and HNO₃. A comparison of mean day and night values at the NF site showed that NH₄⁺, NO₃⁻, and SO₄²⁻ were all lower during the daytime and higher at nighttime. However, measurements at the SF site displayed an opposite trend compared with those at the NF site. Thus, to understand the different trends between NF and SF sites, statistical tests were conducted (see Table 4).

Table 4. Statistical tests for each NH_4^+ and acidic ions at the NF and SF sites.

Time	Statistical values	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-
Day	DF	39	43	15	20
	<i>t</i> value	0.087	0.75	0.273	1.29
	<i>t</i> critical (two-tail)	2.022	2.02	2.132	2.086
	<i>p</i> value (two-tail)	0.931	0.46	0.789	0.212
Night	DF	45	44	25	22
	<i>t</i> value	1.641	1.452	0.446	0.59
	<i>t</i> critical (two-tail)	2.014	2.015	2.059	2.074
	<i>p</i> value (two-tail)	0.108	0.154	0.659	0.561

Two sample *t* tests aimed at testing differences in mean of NH_4^+ and acidic ions between both sites were conducted for the daytime and nighttime, respectively. In all cases, *p* values between both sites were higher than 0.05, 95% significant level. The statistical tests showed no significant differences between NH_4^+ and acidic ion concentrations at the two sites. Similarly, there were no statistically significant differences between the measured NH_4^+ and acidic ions during daytime and nighttime at the NF and SF sites.

However, even if particulate pollutants between the NF and SF sites are not significantly different, they showed opposite trends in the aerosol constituents. Thus, the NH_4^+ concentration differences between NF and SF were plotted, along with wind direction during day and night, to analyze the wind direction effect on these opposite trends (see Figure 6). Only the NH_4^+ concentration difference was plotted because acidic particulates generally have the same trends as NH_4^+ trend. During nighttime, higher positive differences, NH_4^+ concentrations at

Table 5. Equivalent ratios of $\text{NH}_4^+/\text{SO}_4^{2-}$, $\text{NH}_4^+/\text{NO}_3^-$, and $\text{NH}_4^+/(\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-)$.

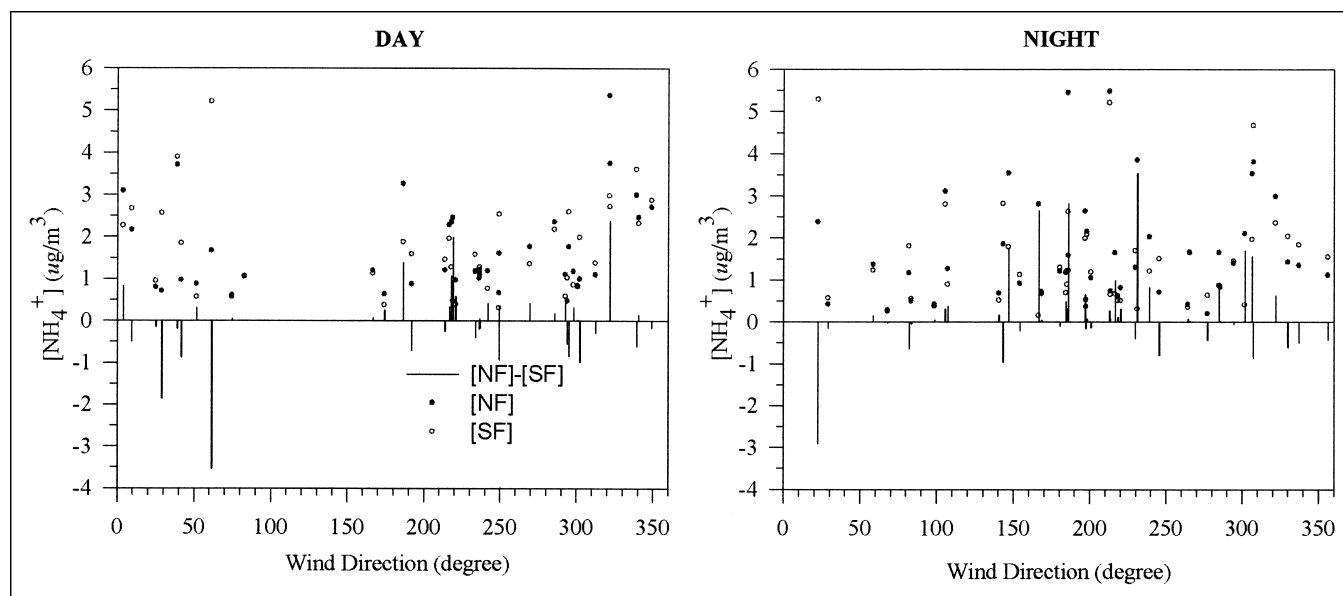
Site	Time	$\text{NH}_4^+/\text{SO}_4^{2-}$	$\text{NH}_4^+/\text{NO}_3^-$	$\text{NH}_4^+/(\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-)$
NF	mean	1.39	3.97	0.99
	day	1.38	4.19	1
	night	1.41	3.78	0.98
SF	mean	1.32	3.61	0.93
	day	1.25	4.2	0.93
	night	1.42	3.09	0.94

NF greater than at SF, occurred during southerly wind because NF site was affected from the nearby waste lagoon. On the other hand, when there was a northerly wind direction at nighttime, higher NH_3 concentrations occurred at the SF site.

Composition of Aerosols

Particulate $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 formations depend on the quantities of NH_3 , acid precursors (i.e., SO_2 and NO_x) present, and the meteorological conditions. Thus, in the systems related to NH_3 , H_2SO_4 , HNO_3 , and water droplets, the composition of aerosols in the atmosphere may be influenced by the characteristics of the experimental sites. Using the data measured from an NH_3 -rich environment (i.e., a commercial hog farm in eastern North Carolina), the constituents of aerosols can be analyzed in a meaningful manner by examining the equivalent ratios of $\text{NH}_4^+/\text{SO}_4^{2-}$ and $\text{NH}_4^+/\text{NO}_3^-$, and $\text{NH}_4^+/(\text{SO}_4^{2-} + \text{NO}_3^- + \text{Cl}^-)$; Table 5).

Equivalent $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios are expected to range from 0.5 to 1 (i.e., the molar $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios are expected to range from 1 to 2), corresponding to a

**Figure 6.** NH_4^+ concentration differences between the NF and SF sites by wind direction at day and night.

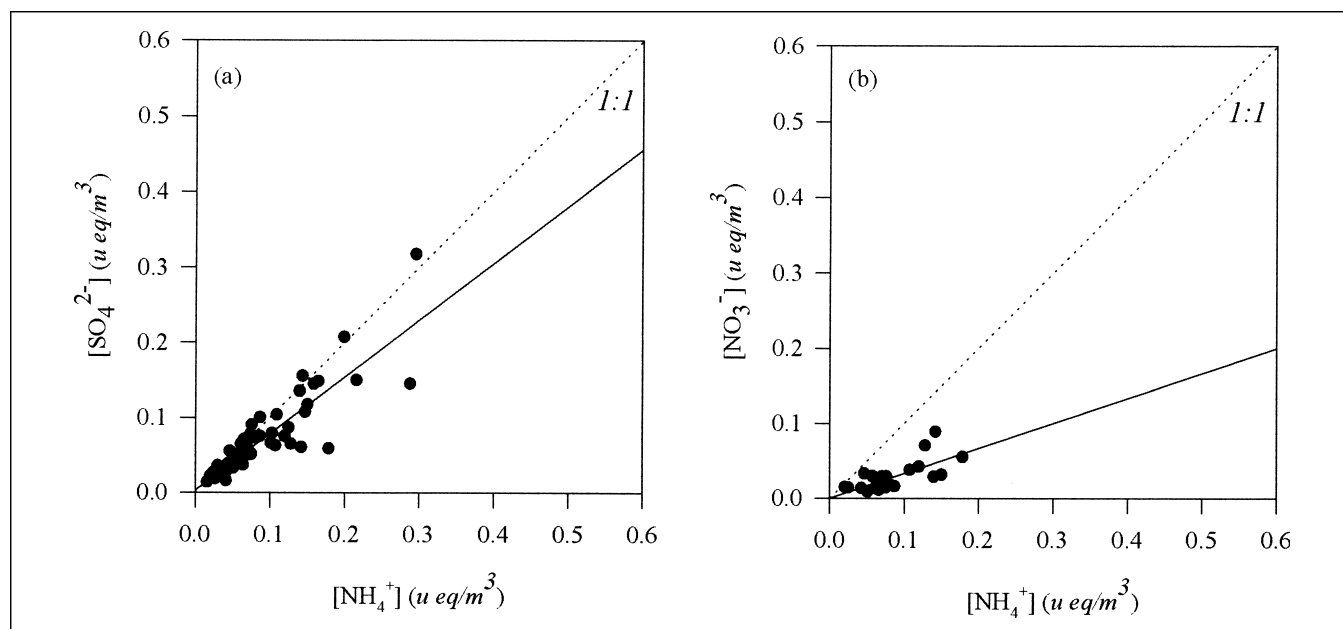


Figure 7. Charge balance between particulate ion and NH_4^+ equivalent concentrations from April to July 1998 at the SF site: (a) $[\text{NH}_4^+]$ vs. $[\text{SO}_4^{2-}]$. (b) $[\text{NH}_4^+]$ vs. $[\text{NO}_3^-]$.

composition intermediate between NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$.^{1,11} Larger observed equivalent $\text{NH}_4^+/\text{SO}_4^{2-}$ ratios here suggest that this site is located in the predominant NH_3 -rich environment. This excess NH_4^+ must be assigned to the presence of HNO_3 and HCl , which also binds some NH_3 . These results indicate that all particulate SO_4^{2-} , NO_3^- , and Cl^- ions were associated with NH_4^+ and that some excess NH_4^+ remained, leaving a base-rich environment in the PM. In the agricultural source region of eastern North Carolina, a large fraction of the inorganic aerosol represents $(\text{NH}_4)_2\text{SO}_4$.

In Figure 7, a linear regression of SO_4^{2-} and NO_3^- concentrations against NH_4^+ concentration during April through July 1998 at the SF site shows good correlations (SO_4^{2-} versus NH_4^+ , $R^2 = 0.756$; $p < 0.05$, and NO_3^- versus NH_4^+ , $R^2 = 0.490$; $p < 0.05$). In this section, because of similar patterns at both sites, only the SF site is shown. A linear regression of the sum of particulate SO_4^{2-} , NO_3^- , and Cl^- concentrations against NH_4^+ concentrations improved the correlation ($R^2 = 0.729$; $p < 0.05$; see Figure 8). Thus, these regressions indicate that all SO_4^{2-} , NO_3^- , and Cl^- were associated with NH_4^+ . Table 6 compares and contrasts the inorganic component abundances in PM_{fine} in agricultural eastern North Carolina to several (urban, rural, remote, and marine) locations. SO_4^{2-} is the most conspicuous constituent of all aerosols considered in Table 6 except the marine aerosol, whose mass is dominated by sodium chloride (NaCl), and also Case II (agricultural North Carolina), whose mass is dominated by NH_4NO_3 . The origin of SO_4^{2-} over the continents is primarily gas-to-particle conversion of SO_2 .¹ The

S content of the Earth's crust is too low for soils to provide a significant source of SO_4^{2-} . Moreover, the mass concentration of PM_{fine} in agricultural eastern North Carolina (i.e., NH_3 -rich) may be similar to those in urban locations.

Figure 9 showed the distribution between particulate NO_3^- and SO_4^{2-} in acidic aerosols at both sites. Based on the results of case studies (see Figure 5), it can be stated that each case might have different air masses. The aerosols in high $[\text{SO}_4^{2-}]$ and low $[\text{NO}_3^-]$ can be representative of aerosols being transported long distances and the case

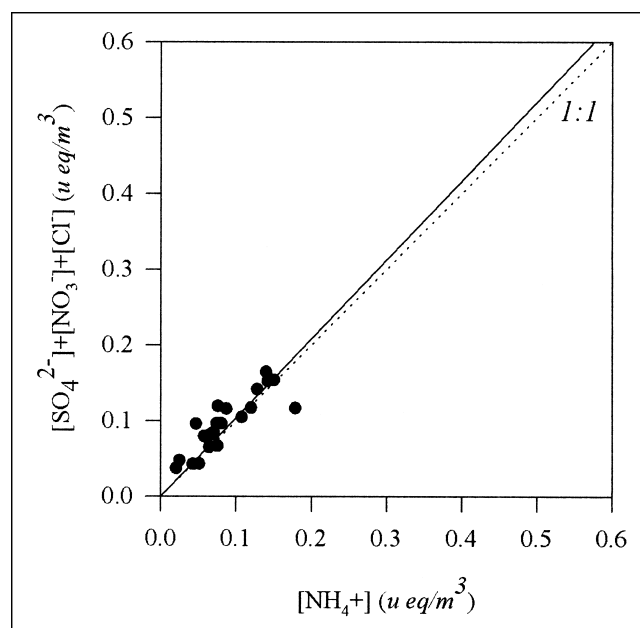


Figure 8. Charge balance between sum of SO_4^{2-} , NO_3^- , and Cl^- and NH_4^+ equivalent concentrations from April to July 1998 at the SF site.

Table 6. Mass concentration ($\mu\text{g}/\text{m}^3$) of inorganic components in PM_{10} in agricultural eastern North Carolina compared with several (urban, rural, remote, and marine) locations.

	Agricultural—Eastern North Carolina ^a		Urban		Remote—Ny-Alesund ^c			
	Case I: Continental Air Mass	Case II: Marine and Agricultural Air Mass	Tees-Side ^e	West Covina ^f	Rural—Wank, Central Europe ^b	With Sea Influence	Without Sea Influence	Marine—Central Atlantic ^d
SO_4^{2-}	14.17	1.93	13.8	16.47	3.15	1.95	2.32	2.577
NO_3^-	1.81	23.95	3	9.7	0.92	0.022	0.055	0.05
Cl^-	0.58	0.65	3.18	0.73	0.112	0.174	0.013	4.625
NH_4^+	4.52	7.87	4.84	6.93	1.295	0.152	0.226	0.162

Sources: ^aAgricultural, eastern North Carolina, this study; ^bRural, Mountain Station (1780 m MSL) in Northern Alps near Garmish, Germany,²²; ^cRemote²³; ^dMarine²⁴; ^eIndustrial area of Middlesbrough in northeastern England (summer); ^fGreater Los Angeles (summer)²¹.

of low $[\text{SO}_4^{2-}]$ and high $[\text{NO}_3^-]$ can be representative of locally produced particulate.

Effects of Relative Humidity

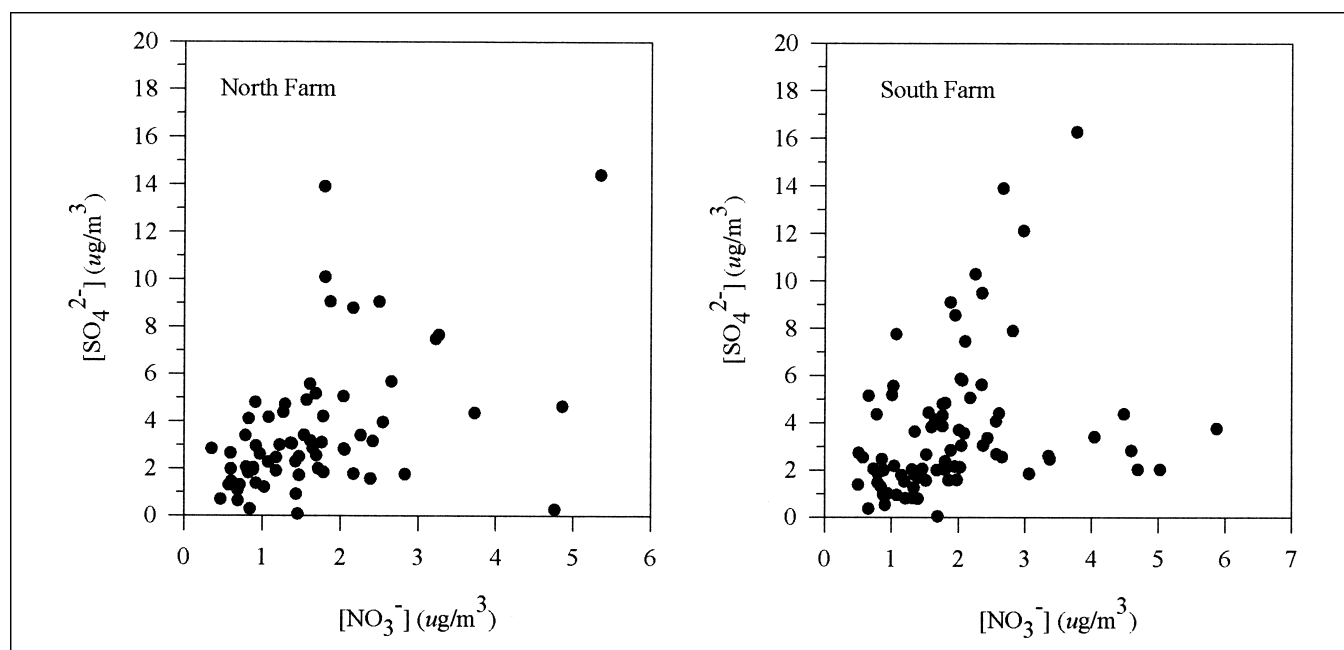
Under high RH conditions, the liquid water content of PM increases the absorbing capacity of the aerosol with regard to gaseous HNO_3 and H_2SO_4 under higher RH.⁵ Because NH_3 is a major factor in the neutralization of these acid gases, RH can affect the NH_4^+ concentration by the neutralization of acid gases in the aerosol fraction. To examine the effects of RH on the production of NH_4^+ , the data were categorized into five RH classes (0–60%, 60–70%, 70–80%, 80–90%, and 90–100% RH). Figure 10 shows the cumulative frequency distribution of NH_4^+ by these five classes.

NH_4^+ concentrations in the >60% RH class were considerably higher at both sites. Higher humidity is, in

fact, expected to facilitate NH_4^+ formation by the growth of condensation of NH_3 with respect to the gaseous HNO_3 and H_2SO_4 . From Figure 10, 60% RH was selected as a criterion to examine RH effects, and gaseous and particulate pollutants for high (>60%) and low (<60%) RH were examined. In Figure 11, gaseous pollutant trends showed higher concentrations at low RH and lower concentrations at high RH. However, the particulate pollutants illustrated the opposite trend, higher at high RH and lower at low RH. Thus, the condensation processes of NH_3 with H_2SO_4 , HNO_3 , and HCl occurred and particulate concentrations were increased because of the gaseous condensation processes with liquid water at high RH.

CONCLUSIONS

Analysis of NH_3 , acid gases, and fine aerosols showed interesting characteristics in this NH_3 -rich environment.

**Figure 9.** The distribution of particulate NO_3^- and SO_4^{2-} concentrations from April to July 1998 at the NF and SF sites.

Gaseous NH_3 concentrations showed higher values during spring and summer. SO_2 had peak values during the winter, which can be attributed to increased fuel usage during these months. HNO_3 had no large seasonal changes, with its lowest concentrations in winter and higher concentrations in spring. Measured particulate constituents showed higher peak concentrations during summer, suggesting that the most efficient gas-to-particle conversion occurred during this time period.

The aerosol fraction in this study area was dominated by the $(\text{NH}_4)_2\text{SO}_4$ particle because of the local abundance of NH_3 , and long range transport of $\text{SO}_2/\text{SO}_4^{2-}$. The assimilation of HNO_3 into NH_4^+ aerosols depends largely on the amount of H_2SO_4 associated with the neutralization with NH_3 . Thus, the sample containing high SO_4^{2-} and low NO_3^- concentration could be representative of aerosols transported over a long distance or precursors from a continental air mass, whereas samples containing low SO_4^{2-} and high NO_3^- concentration could be representative of local area biogenic NO_x emissions leading to NO_3^- or marine air masses having high Cl^- concentrations. The mass concentration of PM_{fine} in agricultural eastern North Carolina (i.e., NH_3 -rich) may be similar to those in urban locations.

From the analysis of RH effects, NH_4^+ concentration was characterized for observations in which RH exceeded 60%. The precursor air pollutants of concern and their

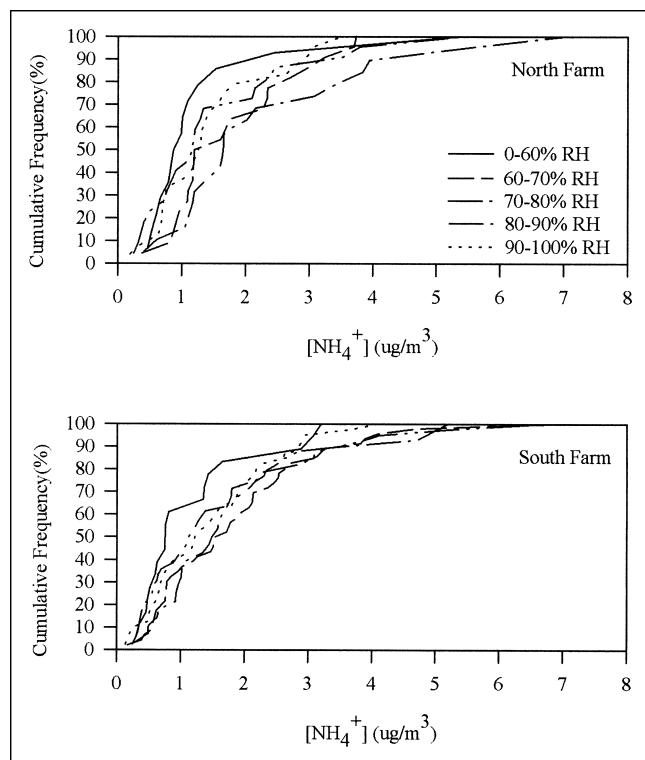


Figure 10. Cumulative frequency distributions of NH_4^+ concentration by five RH classes at the NF and SF sites.

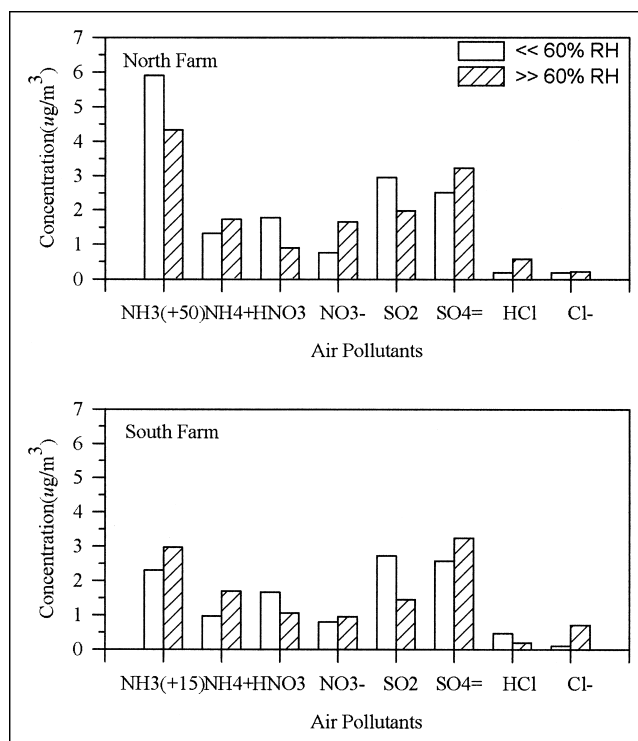


Figure 11. Comparison between a precursor and secondary air pollutant by RH at the NF and SF sites.

respective secondary pollutants displayed opposite concentration trends over this humidity range. The neutralization of NH_3 by HNO_3 and H_2SO_4 was enhanced at RH greater than 60%, as a function of the increased absorbing capacity of the aerosols.

ACKNOWLEDGMENTS

This research has been funded through a cooperative agreement with the Division of Air Quality, North Carolina Department of Environment and Natural Resources, under Contract EA01001. The authors thank George Murray of the North Carolina Division of Air Quality, North Carolina State University Air Quality Research Group, and all of the people who helped them. They are grateful to the North Carolina Division of Air Quality for their valuable field measurements and technical support. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

REFERENCES

- Warneck, P. *Chemistry of the Natural Atmosphere*; International Geophysics Series 41; Academic Press: New York, 1988; pp 313-326, 422-483.
- Meng, Z.; Dabduh, H.; Seinfeld, J.H. Chemical Coupling between Atmospheric Ozone and Particulate Matter; *Science* **1997**, *277*, 116-119.
- Baek, B.H. Measurement, Analysis, and Modeling of Gas-to-Particle Conversion between Ammonia, Acid Gases, and Fine Particles. Ph.D. dissertation. North Carolina State University, Raleigh, NC, 2001; p 191.

4. Baek, B.H.; Aneja, V.P. Chemical Coupling between Ammonia, Acid Gases, and Fine Particles; *Environ. Pollut.*, in press.
5. Stelson, A.W.; Seinfeld, J.H. Relative Humidity and pH Dependence of the Vapor Pressure of Ammonium Nitrate-Nitric Acid and Solutions at 25 Degree Celsius; *Atmos. Environ.* **1982**, *16*, 993-1000.
6. Seinfeld, J.H.; Pandis, S.N. *Atmospheric Chemistry and Physics from Air Pollution and Climate Change*; Wiley & Sons: New York, 1998; pp 523-544.
7. Seinfeld, J.H. *Atmospheric Chemistry and Physics of Air Pollution*; Wiley & Sons: New York, 1986; 377-378.
8. Pacyna, J.M.; Benson, S. Gas-to-Particle Conversion of Sulfur and Nitrogen Compounds as Studied at Marine Stations in Northern Europe; *Atmos. Environ.* **1996**, *30* (18), 3129-3140.
9. Stelson, A.W.; Freidlander, S.K.; Seinfeld, J.H. A Note on the Equilibrium Relationship between Ammonia and Nitric Acid and Particulate Ammonium Nitrate; *Atmos. Environ.* **1979**, *13*, 369-371.
10. Cadle, S.H.; Countess, R.J.; Kelly, N.A. Nitric Acid and Ammonia in Urban and Rural Locations; *Atmos. Environ.* **1982**, *16* (10), 2501-2506.
11. Lee, H.S.; Wadden, R.A.; Scheff, P.A. Measurement and Evaluation of Acid Air Pollutants in Chicago Using an Annular Denuder System; *Atmos. Environ.* **1993**, *27A* (4), 554-553.
12. Aneja, V.P.; Murray, G.C., Jr., Southerland, J. In: *Workshop on Atmospheric Nitrogen Compounds: Emission, Transformation, Deposition, and Assessment*; Raleigh, NC, March 1997; p 299.
13. Aneja, V.P.; Chauhan, J.P.; Walker, J.T. Characterization of Atmospheric Ammonia Emissions from Swine Waste Storage and Treatment Lagoons; *J. Geophys. Res.* **2000**, *105* (D9), 11,535-11,545.
14. Aneja, V.P.; Roelle, P.A.; Murray, G.C.; Southerland, J.; Erisman, J.W.; Fowler, D.; Asman, W.A.H.; Patni, N. Atmospheric Nitrogen Compounds II: Emissions, Transport, Transformation, Deposition and Assessment; *Atmos. Environ.* **2001**, *35*, 1903-1911.
15. Batty, R.; Batty, W.; Overcash, C.; Fudge, S. *Development and Selection of Ammonia Emission Factors*; EPA Contract 68-D3-0034; U.S. Environmental Protection Agency: Research Triangle Park, NC, 1994.
16. McCulloch, R.B.; Few, G.S.; Murray, G.C., Jr.; Aneja, V.P. Analysis of Ammonia, Ammonium Aerosols and Acid Gases in the Atmosphere at a Commercial Hog Farm in Eastern North Carolina, USA; *Environ. Pollut.* **1998**, *102* (S1), 263-268.
17. Possanzini, M.; Febo, A.; Liberti, A. New Design of a High Performance Denuder for the Sampling of Atmospheric Pollutant; *Atmos. Environ.* **1983**, *17*, 2605.
18. *Determination of the Strong Acidity of Atmospheric Fine-Particle (<2.5 μm) Using Annular Denuder Technology*; EPA/600/R-93/037; U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory: Research Triangle Park, NC.
19. Kim, Y.P.; Seinfeld, J.H. Atmospheric Gas-Aerosol Equilibrium I. Thermodynamic Model; *Aerosol Sci. Technol.* **1993**, *19*, 157-181.
20. Walker, J.T.; Aneja, V.P.; Dickey, D.A. Atmospheric Transport and Wet Deposition of Ammonium in North Carolina; *Atmos. Environ.* **2000**, *34*, 3407-3418.
21. Eggleton, A.E.J. The Chemical Composition of Atmospheric Aerosols on the Tees-Side and Its Relation to Visibility; *Atmos. Environ.* **1969**, *3*, 355-372.
22. Stelson, A.W.; Seinfeld, J.H. Chemical Mass Accounting of Urban Aerosols; *Environ. Sci. Technol.* **1981**, *15*, 671-679.
23. Reiter, R.; Sladkovic, R.; Potzl, K. Chemical Components of Aerosol Particles in the Lower Troposphere above Central Europe Measured under Pure-Air Conditions; *Atmos. Environ.* **1976**, *10*, 841-853.
24. Heintzenberg, J.; Hanson, H.C.; Lannefors, H. The Chemical Composition of Arctic Haze at Ny-Alesund, Spitzbergen; *Tellus* **1981**, *33*, 162-171.
25. Gravenhorst, G. The Sulfate Component in Aerosol Samples over the North Atlantic; *Meteor Forschungsber.* **1975**, *10*, 22-33.

About the Authors

Bok Haeng Baek was a graduate research assistant and Viney P. Aneja is a professor in the Department of Marine, Earth, and Atmospheric Sciences at North Carolina State University in Raleigh, NC. Bok Haeng Baek is currently an assistant research scientist at Texas A&M University in Amarillo, TX. Address correspondence to Viney P. Aneja, fax: (919) 515-7802; e-mail: viney_aneja@ncsu.edu.