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Analysis of ammonia, ammonium aerosols and acid gases in the atmosphere at a commercial hog farm in eastern North Carolina, USA

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Abstract

Measurements of atmospheric ammonia, acid gases, and ammonium aerosols were made at a commercial hog farm in Eastern North Carolina, USA, during September through December of 1997. Annular denuder systems (ADS) were used to sample gaseous (hydrogen chloride, nitrous acid, nitric acid, sulfur dioxide and ammonia) and fine aerosol (ammonium, chloride, nitrate, and sulfate) species. Ammonia and ammonium concentrations were determined by colorimetric analysis of the sample extracts. The acid gases and remaining fine particle ionic species were determined by ion chromatographic analysis of the sample extracts. Mean concentrations of the gaseous hydrogen chloride, nitrous acid, nitric acid, sulfur dioxide and ammonia were $0.743\,\mu g/m^3$, $0.255\,\mu g/m^3$, $0.154\,\mu g/m^3$, $2.968\,\mu g/m^3$, and $10.48\,\mu g/m^3$, respectively. Mean concentrations of the fine particle chloride, nitrate, sulfate and ammonium were $0.321\,\mu g/m^3$, $0.548\,\mu g/m^3$, $3.247\,\mu g/m^3$, and $1.102\,\mu g/m^3$, respectively. The fine aerosol fraction was dominated by ammonium sulfate particles. A linear regression of sulfate versus ammonium by equivalent concentration showed a slope of 0.715 and r^2 of 0.88. An emission factor for total ammonia nitrogen flux was estimated using a simple box model as approximately 5 to 10 kg animal^{-1} year^{-1}.

Keywords: Ammonia; ammonium; sulfate; aerosol; emissions

Introduction

Animal production, especially that of hogs, chickens, and turkeys has increased significantly over the last several years in North Carolina and is important to the State's economy (Aneja et al., 1997). The production facilities for these animals, however, have been associated with certain environmental concerns, mainly regarding odor complaints and water run-off problems. However, the atmospheric consequences have largely been ignored thus far (Aneja et al., 1998).
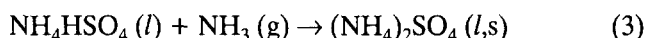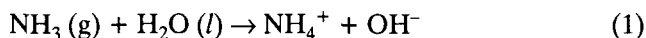
Because of the significant potential for environmental

impact of atmospheric nitrogen, especially ammonia (NH_3) and ammonium (NH_4^+) compounds, the North Carolina Department of Environment and Natural Resources, Division of Air Quality began an examination of these atmospherically related problems in the Fall of 1995. This interest was stimulated by studies suggesting that there may be significant atmospheric deposition of nitrogen compounds in the Neuse River basin and estuary (Paerl, 1995). Atmospheric nitrogen compounds have many sources, both anthropogenic and natural. They are transported by and transformed in the atmosphere before depositing onto sensitive ecosystems.

Once emitted into the atmosphere, NH_3 may undergo conversion to NH_4^+ aerosol. The rate of this conversion, which is largely unknown, will have an important bearing

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on the regional impact of NH_3 emissions. The conversion of NH_3 to NH_4^+ aerosol depends on the concentration of acids in the atmosphere. The following gas (g), liquid (l), or solid (s) phase reactions summarize NH_4^+ aerosol production (Finlayson-Pitts and Pitts, 1986).

$$NH_3 \ (g) + H_2O \ (l) \rightarrow NH_4^+ + OH^- \tag{1}$$

$$NH_3 \ (g) + H_2SO_4 \ (l) \rightarrow NH_4HSO_4 \ (l) \tag{2}$$

$$NH_4HSO_4 \ (l) + NH_3 \ (g) \rightarrow (NH_4)_2SO_4 \ (l,s) \tag{3}$$

$$NH_3 \ (g) + HNO_3 \ (g) \rightleftarrows NH_4NO_3 \ (s) \tag{4}$$

$$NH_3 \ (g) + HCl \ (g) \rightleftarrows NH_4Cl \ (s) \tag{5}$$

While the principal fate of NH_3 in the atmosphere is incorporation into NH_4^+ aerosol by these reactions, approximately 10% is oxidized by the hydroxyl radical ($OH^{\bullet}$) to form an amide radical.

$$NH_3 + OH^{\bullet} \rightarrow NH_2^{\bullet} + H_2O \tag{6}$$
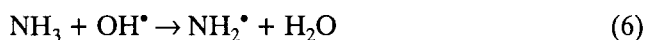
In August, 1997 the Division of Air Quality, along with other research agencies began a study at a commercial hog farm in Eastern North Carolina, where commercial animal production is most concentrated. Average population of the selected farm is 2820 sows and boars, 7520 finishing pigs, and 1410 lactating pigs. Efforts include ambient measurements, and various methods to estimate emission and deposition of nitrogen compounds.

In this paper we present ambient measurements of ammonia, acid gases and fine aerosol species. We estimate ammonia and ammonium emissions from the farm using a simple box model, and compare them with results from other emission studies at this site and other locations.

Experimental

Two ambient sampling enclosures were installed at a commercial hog farm in Eastern North Carolina, 1000 m apart (Fig. 1). The northernmost sampler was located approximately 100 m from the northeast corner of the waste lagoon. The southernmost site was installed near the entrance to the farm. A 12-m tower was installed near the southernmost site. Wind speed, wind direction, and air temperatures were measured at 2 m and 10 m elevation. Relative humidity was measured at 2 m, and solar radiation and precipitation were measured at ground level.

Ambient gaseous hydrogen chloride, nitrous acid, nitric acid, sulfur dioxide, ammonia, and fine aerosol chloride, nitrate, sulfate and ammonium measurements were made at each sampling enclosure using the Annular

Denuder System (ADS) technique (Possanzini, et al., 1983). The annular denuder systems consisted of a cyclone to remove the coarse aerosol fraction ($>2.5\,\mu m$), two annular denuder tubes in series to collect gases of interest, and a filter pack to collect aerosols. Sampling flow rates and intervals were controlled using mass flow controllers and electronic timers, respectively. The specific dimensions of the denuders used in this study were 150 mm by 28 mm with 1-mm annular spaces. The first denuder tube was coated with a solution of 1% glycerine and 1% sodium carbonate (Na_2CO_3) in a 50% mixture of methanol and distilled water to collect acid gases. The second denuder tube was coated with a solution of 2% citric acid in a 50% mixture of methanol and distilled water to collect gaseous ammonia. The filter packs contained a 47-mm Teflon membrane filter, 2.0 μm pore size to collect fine aerosol species. The Teflon filter was followed by a 47-mm nylon filter, 1.0 μm pore size to capture nitric acid from any ammonium nitrate that may have dissociated from the Teflon filter. A 10 ml portion of the coating solution was introduced into the respective denuders, which were then capped and rotated for two
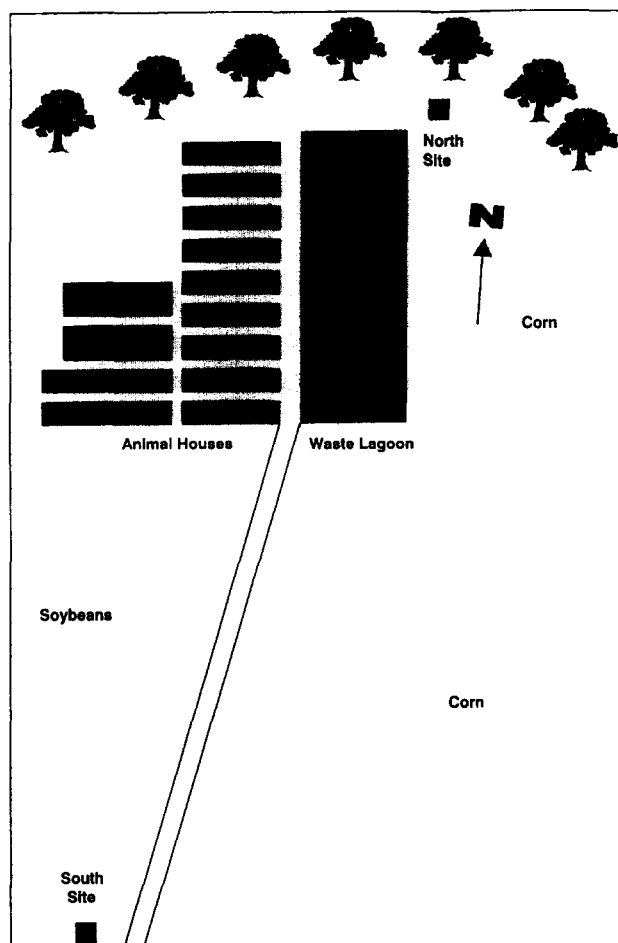

Fig. 1. Layout of hog farm and sampling sites.

Table 1

Summary statistics of gas and fine aerosol species concentrations (μg/m^3)

	HCl	HONO	HNO$_3$	SO$_2$	NH$_3$	Cl$^-$	NO$_3^-$	SO$_4^=$	NH$_4^+$
Mean	0.743	0.255	0.154	2.986	10.48	0.321	0.548	3.247	1.102
Median	0.637	0.226	0.154	1.644	4.722	0.238	0.379	2.458	0.857
1 Std. dev	±0.413	±0.142	±0.008	±3.902	±14.75	±0.327	±0.516	±4.609	±1.464
n	228	101	4	229	223	162	130	203	219
Min	0.321	0.142	0.145	0.199	0.337	0.139	0.147	0.331	0.036
Max	3.513	1.176	0.164	41.76	106.2	2.556	3.472	48.47	14.58

The values below detection limit were not included in these summary statistics.
Standard deviation values were normalized by dividing by $n-1$.

minutes to completely coat the annular surfaces. The tubes were then dried with dry zero air flowing at approximately 2 l/min.

The annular denuder assemblies were transferred to the field in a shipping case and installed in a temperature controlled housing, with the inlet extending from the top of the housing. The sampler inlets were approximately four meters above the ground. The sampler was operated at a constant flow rate of 10.0 l/min. All the ADS measurements were made over 12 hour intervals. The denuder samples were extracted with deionized water. 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 with ion chromatograph eluent (sodium carbonate/bicarbonate solution). Sample extracts were analyzed for chloride, nitrite nitrate, and sulfate by ion chromatography and for ammonium by colorimetric flow injection analysis. Meteorological measurements including wind speed and wind direction were made at two meters and ten meters elevation.

A simple box model was used to estimate emissions of ammonia nitrogen from this site (Finlayson-Pitts and Pitts, 1986). The length of the box was 1000 m, the distance between sampling sites. The width of the box was 200 m, the width component of the waste lagoon, perpendicular to the length of the box, which also encompassed the exhaust fans of the animal houses. A box height of 1000 m was chosen, based on typical daytime planetary boundary layer depth in rural North Carolina (Arya, 1988). Advective flow of ammonia and ammonium into the box was measured at the northernmost site, during sampling intervals when the site was upwind with respect to averaged wind vectors for the interval. Advective flow of ammonia and its reaction product (ammonium) out of the box was measured at the southernmost site during the same sampling intervals.

The mass balance for ammonia or ammonium in the box is given by Sullivan et al. (1996)

$$\frac{dC}{dt} = \left[\frac{vs[C]_{in}}{V} + \frac{JA}{V}\right] = \left[\frac{vs[C]_{out}}{V}\right] + R \qquad (1)$$

where A (m^2) is the surface area covered by the box, V (m^3) the volume of the box, v (m s^{-1}) the wind speed in the box, s (m^2) the cross section area of the box perpendicular to the length of the box, J (μg m^{-2} s^{-1}) the emission flux, $[C]_{in}$ (μg m^{-3}) the ambient concentration at the upwind end of the box, $[C]_{out}$ (μg m^{-3}) the concentration at the downwind end of the box, and R (μg m^{-3} s^{-1}) the chemical production/destruction rate in the box. For a well mixed box $[C]_{out}$ may be assumed to be equal to the concentration everywhere in the box. Finally, at steady state the change of concentration with regard to change in time goes to zero. R is computed using eq. 1 for ammonium values.

Results and discussion

The mean, median, standard deviation, and ranges of concentrations of gaseous hydrogen chloride, nitrous acid, nitric acid, sulfur dioxide, ammonia, and fine-particle chloride, nitrate, sulfate and ammonium are given in Table 1. The mean concentrations for the gaseous hydrogen chloride, nitrous acid, nitric acid, sulfur dioxide and ammonia for all sampling periods, September, 1997 through December, 1997 were 0.743 ± 0.413 μg/m^3, 0.255 ± 0.142 μg/m^3, 0.154 ± 0.008 μg/m^3, and 2.968 ± 3.902 μg/m^3, and 10.48 ± 14.75 μg/m^3, respectively. Nitrous acid concentrations were consistently higher for nighttime samples (0.153–1.176 μg/m^3) than for daytime samples (0.146–0.373 μg/m^3).

The fine aerosol fraction was dominated by ammonium sulfate. The mean concentrations of aerosol species chloride, nitrate, sulfate, and ammonium were 0.321 ± 0.327 μg/m^3, 0.548 ± 0.516 μg/m^3, 3.247 ± 4.609 μg/m^3, and 1.102 ± 1.464 μg/m^3, respectively.

The statistical distributions of ammonia, fine particle ammonium and fine particle sulfate were skewed to the
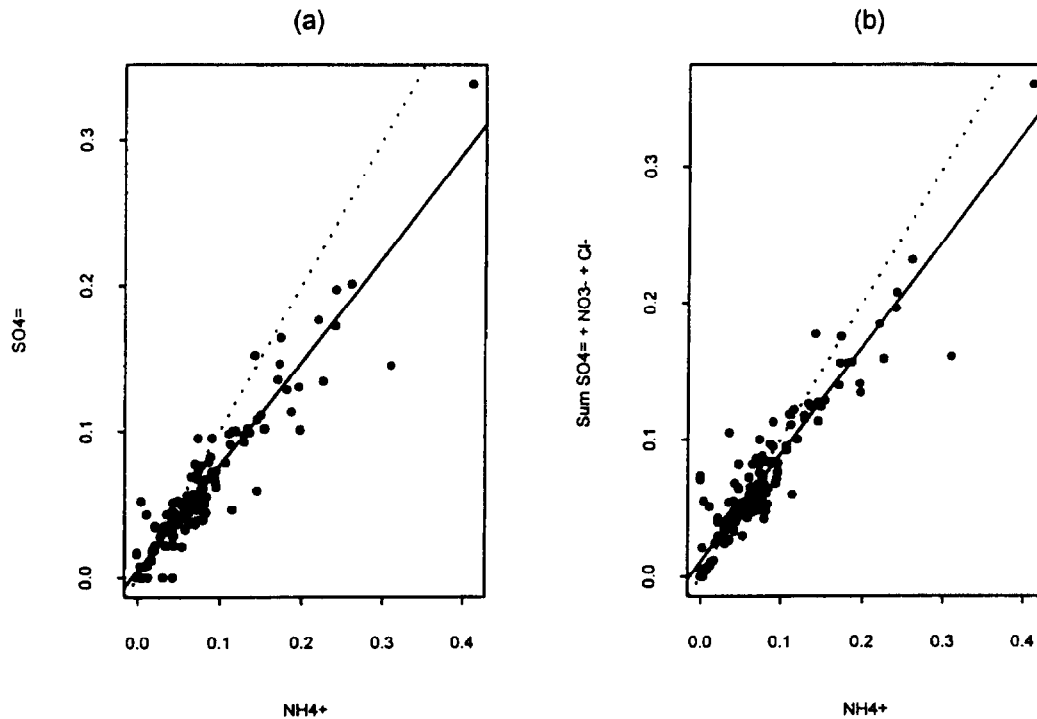
Fig. 2. Charge balance between anions and ammonium using scatter plots: ammonium vs. sulfate (a) and ammonium vs. the sum of anions, sulfate, nitrate and chloride (b) expressed in equivalent concentration (μeq/m^3).

right, thus the mean values were greater than the median values. The minimum and maximum values for ammonia were 0.337 and 106.2; ammonium varied between 0.036 and 14.58; the sulfate range was 0.331 to 48.47. The remaining species were more normally distributed.

Typical ambient concentrations of hydrogen chloride have not been well established but are probably in the low ppb range (Okita et al., 1974). Ambient concentrations of nitrous acid may typically range from <0.1 μg/m^3 to 1.5 μg/m^3 in rural continental areas (Platt and Perner, 1980). Nitric acid concentrations typically are between 1 and 2 μg/m^3 (Cadle et al., 1982). Typical ranges for sulfur dioxide and fine particle sulfate are 1–50 μg/m^3, and 69 μg/m^3, respectively (Mueller et al., 1980). Continental concentrations of ammonia and ammonium, estimated from a model distribution assuming a uniform background mixing ratio superimposed by a boundary layer component, are 2.5 and 3.5 μg/m^3, respectively (Warneck, 1988).

A linear regression of sulfate equivalent concentrations against ammonium equivalent concentrations shows good correlation (r^2 = 0.88), and a regression equation of Y = 0.0046 + 0.7147X (Fig. 2). The domain was restricted to values of ammonium <0.8 μg/m^3 because of two outliers. A linear regression of the sum of sulfate, nitrate, and chloride equivalent concentrations against ammonium equivalent concentration improved the correlation between the measured anions and ammonium. The coefficient of determination was r^2 = 0.87 with

Table 2

Regression statistical test results for ammonium vs. anions

Sulfate vs. ammonium		Sum of anions vs. Ammonium	
	t-value/standard error		t-value/standard error
y-intercept	3.12/0.0015	y-intercept	6.32/0.0017
slope	42.32/0.017	slope	39.32/0.020

a regression equation of Y = 0.0109 + 0.7846X. X is the value of the ammonium concentration expressed in equivalent concentration and Y is the value of the corresponding measured anions in equivalent concentration. The statistical tests for the slope and intercept terms were statistically significant (p < 0.001). The test statistics for the terms in the regression are given in Table 2. The residual standard errors for the sulfate regression and the added anions were 0.01428 and 0.01687, respectively. These regressions indicate that all sulfate, nitrate, and chloride particles were associated with ammonium and that some excess ammonia remained, leaving a base-rich environment.

Ammonia nitrogen emissions were estimated using 12 hour averaged air concentrations of ammonia and ammonium applied to a box model with the wind speed and wind direction measurements. The sample data set available for this exercise, based on the time averaged wind vectors that corresponded to the direction from the

Table 3

Ammonia nitrogen emissions estimates

	Area Flux[3]	Emission Factor[4]
Aneja et al. (1998)[1]	3500–7500	4.5–9.0
Asman and van Jaarsveld (1992)	NA	4.30–13.28
Battye et al. (1994)	NA	7.58
Harper and Sharpe (1998)	NA	2.3
van der Hoek (1998)	NA	5.26–13.53
This Study[2]	546–1064	4.88–9.52

[1]Emissions from waste lagoon only; summer measurements only; emission factor calculated from lagoon dimensions and farm population information.
[2]Emissions from waste lagoon, animal houses and surrounding crops.
[3]Area fluxes are given in μg Nitrogen m^{-2} min^{-1}.
[4]Emission factors are given in kg Nitrogen $animal^{-1}$ $year^{-1}$.

northernmost sampling site to the southernmost sampling site was limited. Because the sites were installed after the prevailing regional winds had shifted to the northeast, no concentration data were available for the opposite wind direction during 1997.

Average wind speeds greater than approximately 1.5 m s^{-1} were required to overcome the effects of trees near the northernmost site. Under low wind speeds, ammonia emissions from the waste lagoon can be swept back toward the northernmost sampling site, resulting in elevated concentrations and a negative difference for ammonia concentrations along the length of the box.

The estimated ammonia nitrogen flux for the entire area under the box is 5459 μg m^{-2} min^{-1} to 10644 μg m^{-2} min^{-1}. The estimated annual emission factor per animal is 4.88 kg $animal^{-1}$ $year^{-1}$ to 9.52 kg $animal^{-1}$ $year^{-1}$.

Aneja and Murray (1998) and other researchers measured emission fluxes from the same waste lagoon, measuring 100 × 250 m, during the same time period. The flux estimate in this analysis includes emissions from several sources: the waste lagoon, the animal houses, and the soil and crops inside the box, whereas the emission flux estimated by Aneja and Murray (1998) represents only the waste lagoon as a source. Taking the different surface areas of concern into account, the two studies gave similar emissions estimates. The estimated range of emissions per animal is also consistent with the ranges proposed by Asman and van Jaarsveld (1992) and van der Hoek (1998), and envelopes the factor proposed by the U. S. Environmental Protection Agency (Battye et al., 1994).

Conclusions

Measured concentrations of gaseous hydrogen chloride, nitrous acid, nitric acid, and sulfur dioxide were generally within typical ambient background concentrations or lower for rural regions. Ammonia concentrations (0.337–106.2 μg/m^3) were elevated above typical ambient levels (2.5–3.5 μg/m^3), suggesting the influence of local ammonia sources. Hydrogen chloride, sulfur dioxide, and ammonia exhibited a high degree of variability between sampling intervals.

Fine aerosol concentrations of chloride, nitrate, sulfate and ammonium were also all within typical ambient background concentrations and highly variable. The aerosol fraction of the samples was dominated by ammonium sulfate due to the local abundance of ammonia.

The simple box model described, using ambient concentration measurements, and wind speed and wind direction data appears to be an effective tool for estimating ammonia emission fluxes from a commercial hog farm.

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