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Atmospheric Ammonia Mixing Ratios at an Open-Air Cattle Feeding Facility

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ABSTRACT

Mixing ratios of total and gaseous ammonia were measured at an open-air cattle feeding facility in the Texas Panhandle in the summers of 2007 and 2008. Samples were collected at the nominally upwind and downwind edges of the facility. In 2008, a series of far-field samples was also collected 3.5 km north of the facility. Ammonium concentrations were determined by two complementary laboratory methods, a novel application of visible spectrophotometry and standard ion chromatography (IC). Results of the two techniques agreed very well, and spectrophotometry is faster, easier, and cheaper than chromatography. Ammonia mixing ratios measured at the immediate downwind site were drastically higher (~2900 parts per billion by volume [ppbv]) than those measured at the upwind site (≤ 200 ppbv). In contrast, at 3.5 km away from the facility, ammonia mixing ratios were reduced to levels similar to the upwind site (≤ 200 ppbv). In addition, PM₁₀ (particulate matter <10 μm in optical diameter) concentrations obtained at each sampling location using Grimm portable aerosol spectrometers are reported. Time-averaged (1-hr) volume concentrations of PM₁₀ approached $5 \times 10^{12} \text{ nm}^3 \text{ cm}^{-3}$. Emitted ammonia remained largely in the gas phase at the downwind and far-field locations. No clear correlation between concentrations of ammonia and particles was observed. Overall, this study provides a better understanding of ammonia emissions from open-air animal feeding operations, especially under the hot and dry conditions present during these measurements.

IMPLICATIONS

The high concentrations of ammonia observed directly downwind of the concentrated cattle feeding operation site are a regionally and globally significant contribution to ammonia concentrations. Very high levels of gas-phase ammonia clearly emitted from this feeding operation may be subject to further law enforcement to prevent a localized health concern for employees of the feeding operation and the nearby community.

INTRODUCTION

Atmospheric ammonia (NH₃) originating from natural and anthropogenic sources plays a key role in the global nitrogen cycle. Atmospheric mixing ratios of NH₃ range from 0.1 to 10 parts per billion by volume (ppbv), depending on proximity to a source.¹ Estimated global NH₃ emissions from the Earth's surface to the atmosphere contribute as much as 54 Tg N/yr.² Approximately 90% of anthropogenic NH₃ originates from agricultural facilities.^{2,3} At concentrated animal feeding operations (CAFOs), which house up to 50,000 cattle in a confined space, high concentrations of gas-phase NH₃ can be observed.^{1,4} In CAFOs, ammonium ions (NH₄⁺) form as a result of the urease-catalyzed microbial hydrolysis of urea and/or uric acid in animal excreta. The NH₄⁺ is subsequently volatilized to gaseous NH₃. Global NH₃ emissions from fertilizer, animal manure application, and stored manure increased from 18 to 34 Tg N/yr between 1970 and 1995 and are predicted to further increase to 44 Tg N/yr by 2030.⁵

Daily formation and emission of NH₃ through agricultural activities are issues of concern to the public and the government for several reasons. At the high concentrations measured in open-air livestock facilities, NH₃ has been linked to odor emissions^{6,7} and human health issues, including respiratory diseases, mucous membrane inflammation syndrome, and asthma.^{8,9} Furthermore, atmospheric enrichment of gas-phase NH₃ and secondary particulate matter (PM) derived from it may have negative impacts on natural environments, such as acid rain,¹⁰ soil acidification,¹¹ groundwater contamination,¹² crop plant toxicity,¹³ and loss of biodiversity.¹⁴ In addition, recent studies on emissions derived from animal feeding operations (AFOs) and the deposition of these suggests that agricultural NH₃ plays an important role in PM_{2.5} (PM <2.5 μm in optical diameter) formation on a regional scale.^{15,16}

Despite increased public concern in the United States, NH₃ emissions and ambient concentrations are currently not regulated under the Clean Air Act, although there are recommended guidelines. These guidelines include limits set by the U.S. Environmental Protection Agency (EPA) (141 parts per billion [ppb]) on the basis of the highest

tested dose per day) and the U.S. Department of Health and Human Services (1700 ppb for acute exposure of 1–14 days and 300 ppb for chronic exposure).¹⁷ Until recently, according to the Comprehensive Environmental Response, Compensation, and Liability Act (CERLA) of 1980, EPA required any facility that released 100 lb of NH₃ in a 24-hr period to report the release. Surprisingly, EPA issued an exemption, effective January 2009, stating that emissions of hazardous materials from animal waste at farms are exception to this rule and do not need to be reported.

Measurement and modeling efforts to characterize agricultural NH₃ emissions (from a wide variety of AFOs) are underway.^{18,19} However, field measurements of NH₃ at agricultural sites, in particular at open-air AFO facilities, are still limited. In fact, only a few studies have been conducted at feedlots representative of the large facilities often found in the southwest United States.^{20,21} One study was conducted at a large open-air facility in the Texas Panhandle, referred to as Feedlot C, where approximately 45,000 head of cattle are housed in 1 mi² (2.6 km²).²² Hourly averaged concentrations of NH₃ approached 700 ppbv. In that study, NH₃ emissions positively correlated with the manure pack temperature but not with air temperature. The activity of microorganisms in the soil and subsequent NH₃ emissions are influenced by the physical properties of the soil, including soil pH, temperature, and moisture.^{23–25}

Emissions of high concentrations of NH₃ may enhance PM formation and deposition in the region.^{26,27} Under typical atmospheric conditions, conversion of NH₃ to the particle phase is likely to occur via reactions between NH₃ and gas-phase inorganics, such as sulfuric acid or nitric acid, to form ammonium sulfate and ammonium nitrate, respectively.^{28,29} Ferm³⁰ estimated that the half-life of NH₃ is 3–6 hr over a distance of 65–130 km depending on the atmospheric mixing ratios of sulfur dioxide (SO₂) and oxides of nitrogen (NO_x; including nitric oxide [NO] and nitrogen dioxide [NO₂]). In this study, measurements in the vicinity of the CAFO were collected in an environment with atmospheric conditions different than most rural or urban environments. In this atypical environment, NH₃ emissions are so high that concentrations of SO₂ and NO_x are limiting with respect to stoichiometric formation of NH₄⁺ salt aerosols. Also, unusually high concentrations of carbon-containing particles are present. The presence of such an extensive amount of organics provides additional surfaces for NH₃ adsorption and absorption under the right conditions.^{31,32} The adsorption and absorption of NH₃ on organic surfaces is maximized at a moisture level of 50–70% in the substrate.³³ Rigorous coincident measurements at the source and downwind but close to the source are required to assess the direct contribution and time scales of NH₃ to PM formation near the source.

In the Koziel study referred to above, gas-phase NH₃ concentrations were determined at a single point on the downwind edge of the CAFO.²² This paper presents more extensive measurements of gaseous and particulate NH₃ species collected at the same 45,000-head feedlot described above (Feedlot C). The concentration of NH₃

species in samples collected at nominally upwind and downwind edges of the facility, as well as far-field measurements collected 3.5 km beyond the downwind edge, are described below. In addition, coincident measurements of PM are reported for each location.

EXPERIMENTAL METHODS

Field Sampling

Several techniques, including scrubbers, denuders, and flux chambers, have been deployed to measure concentrations of NH₃ at AFOs.^{22,27,34,35} NH₃ scrubber measurements have also been performed at a variety of in-house livestock buildings of daily cows, swine, laying hens, and horses.³⁴ This study used a simple sampling apparatus consisting of paired scrubbers, one with a particulate filter upstream of the scrubber and another without (Figure 1). The filter-free sampler collects both gas-phase ammonia, NH₃(g), and particle-phase NH₄⁺, which are collectively referred to as NH_x. Upstream of the second scrubber a glass fiber filter in a nylon housing (McMaster-Carr, Model 4795K3) removes 99.99% of particulates, leaving the gas-phase NH₃. Using the two-scrubber method, the mixing ratios of NH₃(g), total NH_x, and particle-phase NH_x (total – gas) in the ambient air can be determined.

Before sampling, the scrubbers are rinsed twice with d-ionized Millipore water, once with 0.1 M hydrochloric acid (HCl), and again with deionized Millipore water. The scrubbers are then filled with 10 mL of 0.1 M HCl solution for collection of NH₃ species. During operation, the pump is used to vacuum the air at 3 L/min for 20 min, and the solution is drawn from the reservoir through the nozzle and forms a fine aqueous mist sprayed into the chamber. The fine droplets provide a large surface area for efficient collection of NH₃(g). The following reaction occurs, trapping NH₃(g) in solution:



Once formed, the ammonium chloride will remain stable as long as the pH of solution remains below 2.³⁴ To confirm this, the NH₄⁺ concentration in a subset of the samples was determined immediately upon collection, after 24 hr, and after 72 hr, and no change in concentration was observed within experimental uncertainty. This

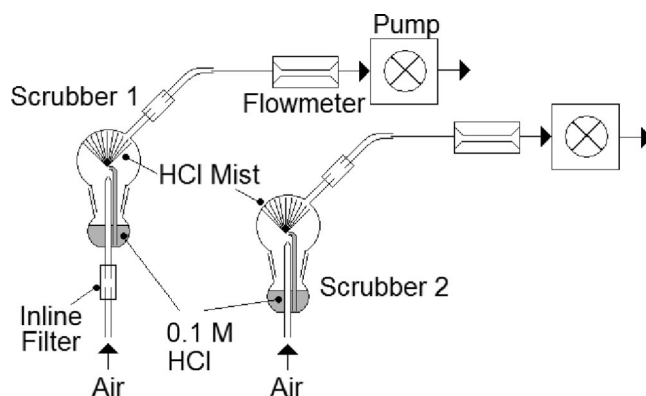


Figure 1. Experimental design for NH₃ sampling. Scrubbers 1 and 2 are used to collect NH₃(g) and total NH_x, respectively.

subset of samples included in the time tests consisted of four laboratory-generated samples, with three replicate measurements conducted for each sample. The sampling of $\text{NH}_3(\text{g})$ and total NH_x in the ambient air was conducted at the nominally downwind and upwind edges of Feedlot C in the summers of 2007 and 2008. This paper primarily focuses on the 2008 campaign, during which a third series of "far-field" samples were also collected from the edge of a dirt road 3.5 km downwind of the feedyard.

For all sampling, the scrubbers were placed 1.5 m above the ground. Routine samples were collected for 20 min at a flow rate of 3 L/min, in the morning (~9:00 a.m.), afternoon (~3:00 p.m.), and evening (~9:00 p.m.). All times are reported as Central Daylight Time (CDT). A total of 161 samples were collected from July 12, 2008 to July 25, 2008.

In addition to NH_3 measurements, measurements of particle size distributions were collected during the project using two Grimm 1.108 portable aerosol spectrometers (PAS). Because $\text{NH}_3(\text{g})$ is a potential source of new particles, it is advantageous to simultaneously measure concentrations of NH_3 and particles to identify correlations between the two.²⁷ The PAS is a laser-based aerosol spectrometer that records a particle size distribution consisting of 15 size bins from 0.35- to 22.5- μm optical diameter every 6 sec.³⁶ Pre- and postcampaign laboratory calibrations of the two PAS instruments used in the field indicated that the instruments were in agreement to within $\pm 3\%$. During these field campaigns, one PAS was continuously operated at the nominally downwind site. The second spectrometer was used to provide coincident size distribution measurements during collection of far-field NH_4^+ samples.

Although prevailing winds at Feedlot C are southerly during the summer, there were some fluctuations in wind direction ($\pm 52^\circ$). Because these deviations translate to longer distances as one moves further from the source, a plume-chasing strategy was devised to target the center of the plume for far-field sampling. A dirt road was used that runs nearly parallel to Feedlot C, 3.5 km away, on the downwind side. The area between Feedlot C and the road was an open field of recently tilled soil. The second Grimm PAS was used to survey particle size distributions along the road.

Before collecting each NH_3 sample at the far-field site, the center of the dust plume from the CAFO was determined 3.5 km downwind. To do so, a series of eight PM samples was collected at prescribed far-field locations along the dirt road to roughly pinpoint the center of the plume at that moment in time. This study was primarily interested in the total volume concentration of PM_{10} (PM <10 μm in diameter) as a function of time and location relative to the CAFO. To obtain the volume concentrations of PM_{10} reported below, only the particle counts in 12 bins of optical diameters 0.35–10 μm were considered. For each bin, the number concentration was converted to a volume assuming that all particles in the bin are spheres with a diameter equal to the average diameter in that bin. The total volumes in bins 1–12 were then summed together to obtain the total volume of PM_{10} . A detailed account of the spatial and temporal variations in size distributions observed at the CAFO is available elsewhere (N. Hiranuma and S. Brooks, manuscript in preparation).

After completing an initial PM_{10} survey, the authors returned to the point where the highest concentration of PM_{10} was measured, assumed this was designated plume center for the given day, and collected NH_3 and total NH_x samples for the standard 20 min at 3 L/min, at 1.5 m above the ground. Coincident PM sampling was also conducted. This plume-chasing procedure was repeated each time a far-field sample was collected.

NH_3 concentrations are influenced by several complex, interrelated variables, including meteorological conditions, soil conditions, and the presence and concentration of aerosol particles, which could provide surfaces for NH_3 adsorption. During this campaign, atmospheric and soil parameters were monitored. An on-site weather station was deployed on a 1.8-m platform at the downwind site to provide measurements of relative humidity (RH), wind direction, ambient temperature, wind speed, and rainfall, recorded every 6 sec. Measurements of soil moisture content and soil temperature at the surface and at a 25-cm depth within the soil were also obtained at the downwind sample site. To check the variability of soil temperature, soil temperature was also measured at three additional locations, two points within the pens located nearby the downwind site and one point at the upwind site. The surface and subsurface measurements at all four sites were consistent throughout the campaign ($\pm 1.3^\circ\text{C}$ standard deviation).

Laboratory Analysis

Scrubber Collection Efficiency. The scrubbers used in this study are built in-house in the Texas A&M Chemistry Glass Shop. Following the method of Schade and Crutzen,³⁴ the collection efficiencies of the scrubbers were tested in the authors' laboratory. As in the field experiments, 10 mL of 0.1 M HCl were placed in each scrubber, and samples were collected for 20 min at 3 L/min. $\text{NH}_3(\text{g})$ was generated by stirring an ammonium sulfate solution (250 mL of 0.01 M ammonium sulfate) and allowing the scrubbers to sample the NH_3 emitted off the solution. After collection, ion chromatography (IC) was used to determine the concentration of NH_3 collected.

All IC analysis was performed on a Dionex System 4000i with a Dionex IonPac CS12 cation exchange column using 18 mM methanesulfonic acid as the eluent solution and 100 mM tetrabutylammonium hydroxide as the cation regeneration solution as specified by the supplier. For these measurements, 1 μL of each standard solution was directly injected into the instrument. To determine if there was any NH_3 emanating from the tubing and filters, solution blanks containing only 0.1 M HCl were also analyzed by IC and none was detected.

One advantage of using IC is that sample solutions collected in the field can be analyzed directly without any preanalysis sample preparation. However, disadvantages are that this method consumes a significant amount of eluent and regeneration solutions, and daily replacement of these solutions is a necessity. Further, a new calibration is required each time the solutions are changed.

Qualitatively speaking, the mass of NH_3 in the sample solution can be converted to an approximate mixing ratio in the air. In the calculation below, two measured values are used, the mass of NH_3 in the solution (M_{NH_3}),

determined by IC or spectrophotometry, and the total volume of air sampled by the scrubber (V_{Air}). Mixing ratios are calculated according to

$$\text{Mixing Ratio NH}_3 \cong \frac{M_{\text{NH}_3}}{V_{\text{Air}} \times n_{\text{Air}} \times m_{\text{NH}_3}} \quad (2)$$

where n_{Air} is the molar concentration of air molecules, which is assumed to be $0.0409 \text{ mol L}^{-1}$ on the basis of standard temperature and pressure, and m_{NH_3} is the molecular mass of NH_3 , 17 g mol^{-1} . It is noted that although this is an adequate method to generate samples containing a range of mixing ratios for comparing two scrubbers or two analytical methods, the mixing ratio is only an estimate, and this is not an appropriate method for direct calibration.

Tests were conducted with multiple scrubbers in parallel and the experimental errors involved in the scrubber sampling, sample preparation, and chemical analysis were examined to define the total uncertainty in this NH_3 detection technique. As a secondary test, each scrubber was also set up with a second scrubber in line at the output of the first scrubber. In each case, the concentration of NH_4^+ in the second scrubber solution in series was below the instrumental detection limit, indicating that the first scrubber in each case was approximately 100% efficient, within experimental uncertainty. A test was also run in which two scrubbers set up in parallel, one scrubber with a filter in the sampling line and a second scrubber with no filter, were used to sample a single source of NH_3 . The measured concentrations agreed (at the 95% confidence level), indicating that no NH_3 is lost because of absorption on the particulate filter.

Finally, parallel experiments were conducted in which one scrubber was filled with deionized Millipore water instead of 0.1 M HCl solution. It was found that the trapping efficiency in water was reduced to less than 30%. This confirmed that it was important to collect field samples into acid solution instead of water.

Spectrophotometric Determination of NH_3 . All samples collected at Feedlot C were stored in a refrigerator and transported to the authors' laboratory at Texas A&M University. Concentrations of $\text{NH}_3(\text{g})$ and total NH_x in solution samples were determined using visible spectrophotometry following a technique developed to measure NH_4^+ concentrations in sea water.^{37,38} To the best of the authors' knowledge, this is the first time that this technique, modified by the authors, has been applied to agricultural air sampling. In this technique, NH_4^+ is complexed with phenol solution, sodium nitroprusside solution, and oxidizing solution, which act as catalysts to form the indophenol complex. The optical absorbance of blue indophenol color formed with NH_4^+ is measured spectrophotometrically at 640 nm. No other peak absorption was observed except the contribution from the water ($\sim 310 \text{ nm}$). The technique was originally developed for ocean water samples, which have a pH of 8.2. Because the reaction forming indophenol will not occur under acid conditions, it was necessary to increase the pH of the field samples (collected and stored at a pH of < 2) by adding

aliquots of 1 M sodium hydroxide (NaOH). Titrations were performed to determine the concentration of NaOH required to ensure an endpoint pH of > 11 . The authors note that the impact of changing pH on outgassing of the NH_3 that had been trapped in the acid was negligible. Tested 72 hr after the neutralization, the NH_3 concentrations were the same as the original measurement concentrations, within the 95% confidence limit. After pH adjustment, the scrubber sample (2.5 mL) was mixed with 0.1 mL of 1 M phenol solution, 0.1 mL of 1 M sodium nitroprusside solution, and 0.25 mL of oxidizing agent. Phenol solution was prepared by dissolving 20 g of analytical-grade phenol in 200 mL of 95% v/v ethyl alcohol. Sodium nitroprusside solution was made by dissolving 1 g of sodium nitroprusside, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2 \text{H}_2\text{O}$, in 200 mL of deionized water. Oxidizing solution was produced by the mixing alkaline reagent and 0.75 M sodium hypochlorite solution in a volumetric ratio of 4:1. Alkaline reagent was generated by dissolving 100 g of sodium citrate and 5 g of NaOH in 500 mL of deionized water and sodium hypochlorite (commercially available Clorox).

After 1 hr in the dark at room temperature, 1.5 mL of solution was transferred into an acrylic cuvette and the absorbance was measured at 640 nm. In these measurements the absorbance was zeroed against a blank standard of deionized Millipore water. It was observed that the standard plus the cuvette absorbed a minor amount, equivalent to approximately $0.7 \mu\text{M}$ NH_3 , which was eliminated by zeroing the instrument. A daily calibration curve was generated using solutions containing 0, 1, 30, 50, 80, and $100 \mu\text{M}$ NH_4^+ standards; the calibration curve was generated daily. For comparison, a calibration was also performed on standards made in deionized Millipore water, and no significant differences in absorbance at 640 nm were observed between the HCl and water standards. Some of the samples contained NH_4^+ concentrations exceeding the upper detection limit of the spectrometer. In these cases, the NH_4^+ solutions were diluted with deionized Millipore water in a ratio of 1:20, and the measurements were repeated.

RESULTS AND DISCUSSION

Comparison between NH_3 Measurement Methods

A series of laboratory samples generated by collecting gas from the headspace over solutions containing NH_4^+ in concentrations of 20–120 μM were analyzed by IC and visible spectrophotometry. Under standard conditions without any dilutions, this translates to atmospheric mixing ratios concentrations of approximately 80–490 ppbv under operating condition used in the field. The results are shown in Figure 2. As described above, blank solutions of 0.1 M HCl not exposed to any $\text{NH}_3(\text{g})$ were also analyzed to check for any interferences. The uncertainty in measurements by IC and visible spectrophotometry are ± 10 and $\pm 18\%$, respectively. Within these uncertainties, the measurements by both methods agree over the full range of concentrations. Thus, the new spectrophotometry method (with the detection limit of $1 \mu\text{M}$) used here is an inexpensive, rapid, and accurate technique for this application. All samples collected in the field as described below were analyzed by spectrophotometry.

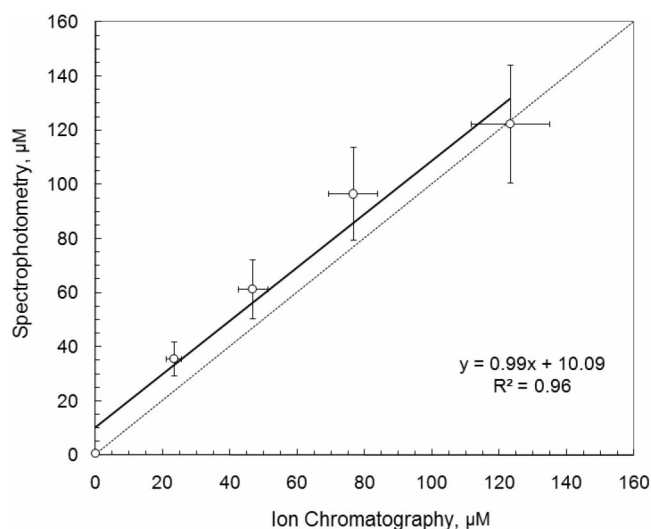


Figure 2. Comparison between IC and visible spectrophotometry measurements for solutions of known concentrations of NH_4^+ .

Field Measurements

Measurements of atmospheric and soil conditions sampled throughout the 2008 campaign are shown in Figure 3, A and B, respectively. Routine samples were collected for 20 min at a flow rate of 3 L/min, in the morning (~9:00 a.m.), afternoon (~3:00 p.m.), and evening (~9:00 p.m.). The wind direction was consistently southerly, with the exception of July 12, 2008. As Figure 3A illustrates, the average wind speed was $3.5 \pm 1.3 \text{ m sec}^{-1}$ and never exceeded 6.3 m sec^{-1} during the project. The average ambient temperature was $25 \pm 5 \text{ }^\circ\text{C}$. Although the overall variation in temperature was small, the range of RH encountered varied greatly (average $58 \pm 20\%$ RH).

During the sampling campaign, one extended period of rainy conditions occurred from July 13–16. In the field, a rain gauge recorded 1, 9.4, 10.3, and 2 mm of rainfall on July 13, 14, 15, and 16, respectively. During the rainy period, the soil moisture content rose to 0.2 v/v (wet basis) (Figure 3B), which is considered fully saturated, on the basis of the porosity of soil.³⁹ The soil remained saturated until 3 days after the rain ended. As illustrated by the PM measurements below, saturated soil conditions are coincident with clean atmospheric conditions, and dusty conditions occur only when the soil moisture has dried out to below 0.2 v/v. Throughout the campaign, a diurnal cycling of the air and surface soil temperatures was observed (Figure 3B). In addition, a routine peak of subsurface soil temperature at the evening was observed under dry conditions.

A time series of the total NH_x and $\text{NH}_3(\text{g})$ concentrations (20-min averages unless otherwise stated) observed at the downwind site during 2008 is shown in Figure 4A. For comparison, the concentrations of PM_{10} measured by the Grimm PAS at the same location during that time are shown in Figure 4B. The mixing ratios of NH_3 species were higher at the downwind site, with campaign averages of total NH_x of 1562 ppbv and $\text{NH}_3(\text{g})$ of 1465 ppbv at the downwind site compared with 194 and 133 ppbv at the upwind site. At the downwind site, a maximum total NH_x mixing ratio of 2947 ppbv was observed on July 16. This was after a day of rain, which moistened the soil and may

have allowed for enhanced microbial activity. Only one downwind sample was collected in which the concentration was in the same range as the upwind samples. This was on July 13, which was an unusual day because the wind was from the north. In general, the NH_x concentration was highly variable throughout the project and did not follow a clear diurnal cycle. Because of the many variables contributing to the concentration of NH_3 observed, the observed variability cannot be attributed to a single parameter during this time period. For example, Todd et al.²¹ noted that ground-level concentrations of NH_3 emitted by cattle feedlots depend strongly on the Monin–Obukhov stability length, which varies widely throughout the day.

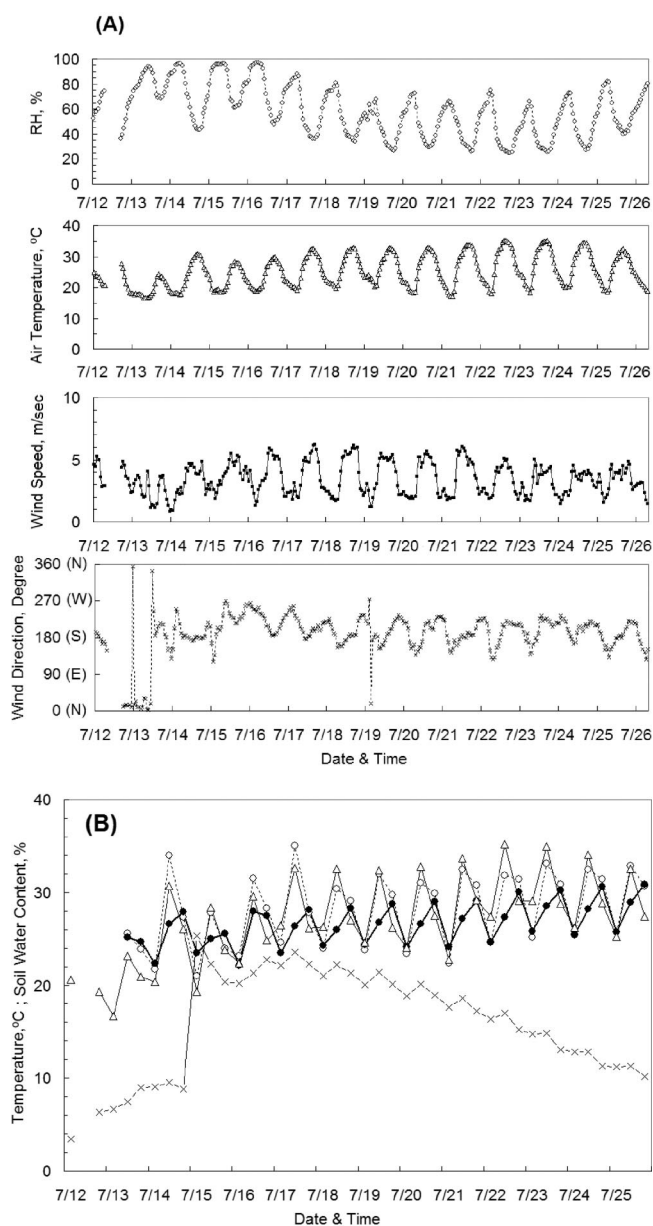


Figure 3. (A) Hourly time-averaged meteorological data, including RH (○), air temperature (Δ), wind speed (■), and wind direction (dashed ×). (B) Measurements of air temperature (Δ), soil temperature at a depth of 5 cm (○), soil temperature at a depth of 25 cm (●), and soil water content at a depth of 25 cm (×) are shown.

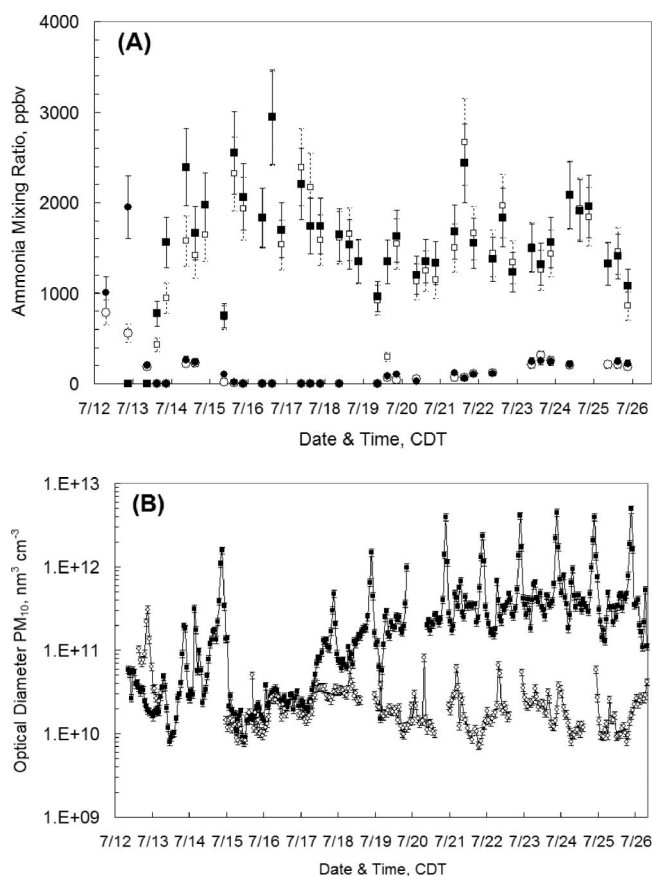


Figure 4. (A) Mixing ratios of total NH_x at the downwind and upwind sites are shown as ■ and ●, respectively. Mixing ratios of NH₃(g) at the downwind sites are shown as □ and ○, respectively. Error bars represent the experimental uncertainty of the spectrophotometric technique (\pm experimental error). (B) Volume concentrations (20-min averages) of PM₁₀ at the downwind (■) and upwind sites (○). Error bars represent the inlet loss rate of the aerosol spectrometer (\pm 10% inlet loss rate).

As seen in Figure 4B, the concentrations of PM₁₀ at the feedlot have a distinct diurnal cycle, with exceedingly high maximum concentrations, relative to PM₁₀ concentrations in other urban and rural environments.⁴⁰ Maximum concentrations of 1-hr averaged PM₁₀ ($>2.5 \times 10^{12}$ nm³ cm⁻³) were observed to occur in the evenings. These peaks are coincident with increases in cattle activity, increased boundary layer stability, and daily minima in the moisture content of the corral surfaces.^{41,42} Additional contributing factors to increased dust concentrations are moisture content of the corral surfaces and changes in the relative temperatures of the air and soil surface. During the daylight hours, the air temperature is warmer than the soil surface. Each evening, the air is cooled to below the temperature of the soil. This evening temperature gradient may enhance the upward flux of dust and NH₃ from the surface. Although this is consistent with the diurnal behavior observed in the aerosol concentrations, no corresponding trend is observed in NH₃ concentrations. Another feature in the diurnal cycle of the hourly averaged PM₁₀ concentrations is the regular occurrence of a smaller but routine peak each morning (PM₁₀ $\sim 10^{12}$ nm³ cm⁻³). This peak coincides with daily arrival of the feed truck and distribution of grain for the morning feeding. Following

precipitation, there is a sudden drop in the concentration of atmospheric coarse particles. Intense rain in a 3-hr period from 1:00 to 4:00 a.m. on July 15 resulted in 6.3 mm of accumulated precipitation. Intense rain showers within such a short period may be a direct trigger of the sudden drop in PM concentration. Clean conditions persisted until the rain stopped and the pen surface dried out (to <0.2 v/v soil moisture) on July 18. Afterwards, the diurnal cycling of coarse particulate volume concentrations were once again observed.

A summary of NH₃(g) and total NH_x samples collected in the morning ($\sim 9:00$ a.m.), afternoon ($\sim 3:00$ p.m.), and evening ($\sim 9:00$ p.m.) is shown in Figure 5. One result illustrated by Figure 5 is that the ambient NH₃ at the feedyard is almost exclusively in gas phase. In some samples, the concentration of NH₃(g) measured were the same as the total NH_x mixing ratios, within the uncertainty of the measurements ($\pm 18\%$), indicating no detectable NH_x at all in the condensed or particle phase. Further evidence that the NH₃ remains in the gas phase under the conditions encountered

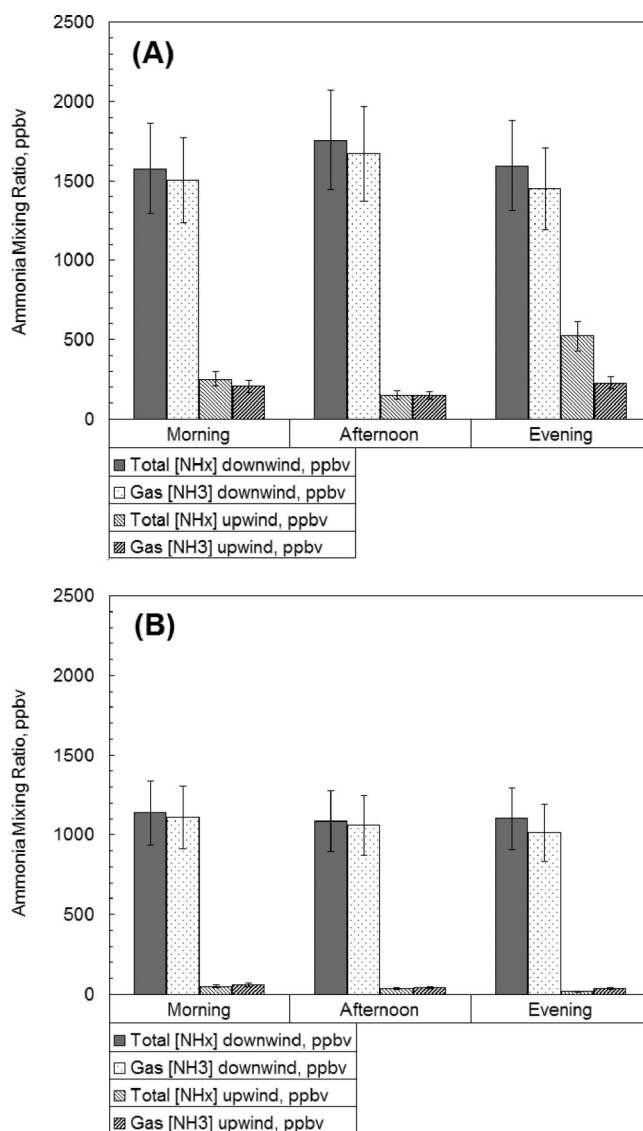


Figure 5. Average NH₃ concentrations measured in (A) 2008 and (B) 2007.

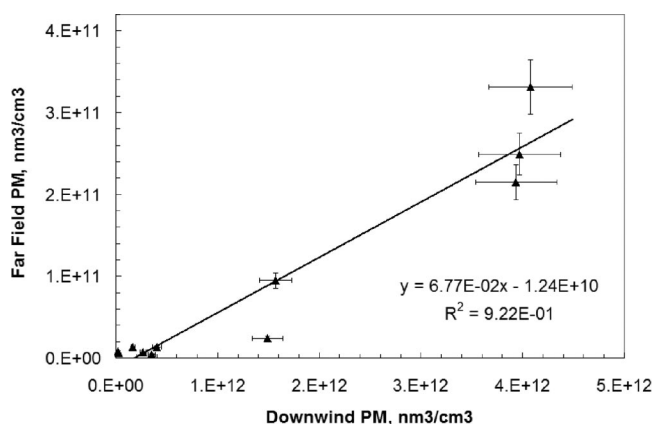


Figure 6. Correlation between 20-min time-averaged concentrations of PM_{10} measured at the downwind and far-field locations.

at Feedlot C can be found in the authors' published work.⁴³ In concurrent work, an elemental analysis was conducted of the particles collected at Feedlot C and found that agricultural aerosols at Feedlot C contain large amounts of carbon but only small amounts of nitrogen-containing species.⁴³ At the RH encountered during this measurement campaign (usually <75%), the particles have not undergone significant deliquescence,⁴³ which is consistent with the limited conversion of NH_3 to the condensed phase.³² The dominance of organic material in particles at Feedlot C is an unusual scenario. According to nationwide Interagency Monitoring of Protected Visual Environments (IMPROVE) network measurements, particle composition in rural areas is typically dominated by ammonium sulfate and ammonium nitrate, although areas closer to urban centers contain increased levels of organic materials.⁴⁴

For comparison, the authors' NH_3 measurements collected in 2007 using the identical method are shown in Figure 5B. In 2007, with a total of 34 samples, an average of 1114 and 33 ppbv NH_x were observed at the downwind and upwind sites, respectively. These values are much lower than the average NH_x mixing ratios reported for 2008, 1562 (downwind) and 194 ppbv (upwind). The observed differences are most likely due to scavenging during the more frequent rain showers during the 2007 campaign. In 2007, it rained 10 of 25 sampling days, amounting to 40.6 mm of rain during the campaign. The average temperature in 2007, 26 ± 3 °C, was similar to the average for 2008, 25 ± 5 °C. In comparison, Koziel reported much lower concentrations of $NH_3(g)$ with an hourly average of 712 ppbv observed at Feedlot C during the spring of 2003.²² However, the authors note that because the time scales differ by a factor of 3 between these measurements and their own, the results are not strictly comparable. Additional measurements are needed to assess the seasonal variability of NH_3 emissions.

Far-Field Sampling of NH_3 and Particulates

Additional far-field measurements were conducted approximately 3.5 km downwind from the feedyard to gain insight into the early stages of NH_3 fate and transport from the lot. As described above, a series of eight measurements of PM concentrations were conducted along the far-field road to identify the location of the aerosol

plume from the feedlot. The success in capturing the aerosol plume is illustrated in Figure 6. In Figure 6, far-field PM_{10} concentrations are plotted against PM_{10} concentrations coincidentally measured at the downwind edge of the feedlot. The average far-field PM_{10} fraction of the PM_{10} measured at the downwind site was calculated as 8.5%, and a linear relationship with a correlation coefficient of $r = 0.9$ was found. This shows that the remnants of the PM plume at approximately 3.5 km are successfully captured and consistently sampled. Although well correlated with the downwind measurements, the far-field PM concentrations were less than 20% of the concentrations at the downwind edge of the CAFO (Figure 7). The decrease in concentration with downwind distance is attributable to a combination of particle settling and plume dispersion. For instance, a 10- μm particle, assuming a soil density of 2.65 g cm^{-3} , has a terminal settling velocity of $\sim 0.8 \text{ cm sec}^{-1}$. Depending on vertical mixing, a large fraction of the 10- μm particles will not reach the far-field site under typical sampling conditions. Overall, the PM measurements indicate successful choices of the far-field sampling site and capture of the plume from the CAFO.

Without any loss by chemical reactions or addition of NH_3 from fresh sources, the NH_3 sampled at the far-field would also be expected to be correlated with the downwind measurements. However, a much weaker correlation is seen between NH_3 concentrations at the edge of the lot and further downwind ($r \leq 0.5$). At 3.5 km, the concentrations of NH_3 are more variable, ranging from approximately 0.1 to 23% of the downwind concentrations. The average far-field mixing ratio at this site was 180 ppbv for total NH_x and 162 ppbv for $NH_3(g)$. These average values match the average mixing ratios at the upwind site, at the 95% confidence level, although less variability was observed at the upwind location. It is noted that an open field of recently tilled soil was between the CAFO and the far-field sampling site, but the field's contribution to the NH_3 plume cannot be quantified from the authors' measurements. Interestingly, at 3.5 km downwind, the NH_3 species are still predominantly in the gas phase.

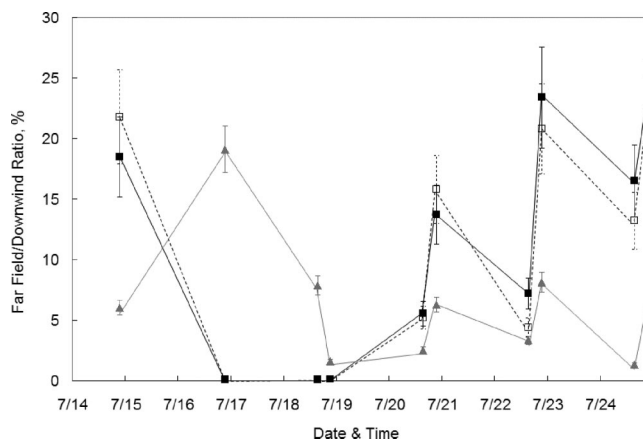


Figure 7. Ratios of concentrations measured at the far-field (~3.5 km downwind) site compared with those measured at the downwind edge of the feedlot for PM_{10} (▲), total NH_x (■), and $NH_3(g)$ (□). Lines connecting the data points are included to guide the eye.

As can be seen in Figure 7, changes in NH_3 concentrations over the 3.5-km distance do not parallel the changes in PM concentrations. It can be seen in the figure that the far-field PM_{10} concentration ratio to downwind can be higher, lower, or similar to the NH_x concentrations. The far-field NH_x and NH_3 ratios do follow similar trends. Thus, under no circumstances should PM be used as a tracer for NH_3 or vice versa. It can be concluded based on these measurements that agricultural NH_3 is almost exclusively in the gas phase near the source under the hot and dry conditions experienced at Feedlot C. Further, the dispersion of the NH_3 is less predictable than that of aerosols. Possible correlations between NH_3 mixing ratios and individual meteorological parameters were explored, but no statistically significant correlation between any single contributing factor and the NH_3 concentration was observed. Elucidation of dependence on these parameters may be possible but will require measurements over a longer period of time and consideration of the combined influences of multiple variables to fully explain the complex variability observed in concentrations of gaseous and total NH_3 species.

More measurements are needed to quantitatively understand the high variability in observed NH_3 concentrations. NH_3 mixing ratios depend on conditions in the soil, where microbial activity is driven by soil temperature, moisture, and pH, and in the air, where the conversion of $\text{NH}_3(\text{g})$ to the particulate phase depends on air temperature, humidity, precipitation, and the presence and composition of pre-existing particles.

CONCLUSIONS

During the summers of 2007 and 2008, total NH_3 and $\text{NH}_3(\text{g})$ were collected at the nominally downwind and upwind edges of a CAFO in the Texas Panhandle, Feedlot C, as well as approximately 3.5 km farther downwind of the lot. Off-line analysis of field samples to determine NH_3 mixing ratios was performed using a new spectrophotometric method. Comparisons showed that results from this method and standard IC agreed very well. The new spectrophotometry approach provides an excellent alternative to IC and is faster, easier, and less expensive than chromatography.

At the downwind edge of the CAFO, exceptionally high mixing ratios of total NH_x were observed, as high as approximately 2900 ppbv averaged over 20 min. At this site, mixing ratios of at least 1000 ppbv of NH_3 were observed under dusty and relatively dust-free conditions. The mixing ratios observed at the upwind location were an order of magnitude lower (≤ 200 ppbv). It is noteworthy that although the concentrations observed at the downwind site of this approximately 45,000-head cattle feeding operation comply with the existing limits set by the U.S. National Institute of Occupational Health and Safety (>35 ppm averaged over 15 min), the daily peaks exceed the worker-exposure guideline set by EPA (141 ppb) and the U.S. Department of Health and Human Services (1.7 parts per million [ppm] for acute exposure of 1–14 days and 0.3 ppm for chronic exposure).¹⁷ Conditions in the atmosphere and in the soil were also measured to explore how these influence NH_3 concentrations.

Possible correlations between NH_3 and NH_x concentrations and meteorological parameters were also explored, but no statistically significant correlation between any single contributing factor and the NH_3 concentration was observed.

In addition, far-field measurements of PM_{10} showed that only up to approximately 20% of aerosol is transported to the site at a distance of 3.5 km away from the lot measured near the ground (1.5 m above the ground). The NH_3 concentrations at the far-field site were also significantly and variably lower than at the edge of the lot, ranging from 0.1 to more than 20% of the concentrations at the downwind edge of the facility, with average concentrations comparable to the upwind site. One unique contribution of this study to the understanding of agricultural NH_3 is that NH_3 emitted from the cattle feeding activities was almost exclusively in the gas phase, even in the presence of extensive particle loadings. Under conditions typically occurring elsewhere in the in the atmosphere, this would be unlikely. However, on the basis of the predominately organic composition and low hygroscopicity of particulates at Feedlot C, the authors conclude that the moisture content of PM during the 2008 project was rarely high enough for significant adsorption and absorption of NH_3 to occur.⁴³ Overall, this study provides a better understanding of NH_3 emissions from an open-air AFO.

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REFERENCES

1. Aneja, V.P.; Nelson, D.R.; Roelle, P.A.; Walker, J.T. Agricultural Ammonia Emissions and Ammonium Concentrations associated with Aerosols and Precipitation in the Southeast United States; *J. Geophys. Res.* **2003**, *108*, 4152; doi: 10.1029/2002JD002271.
2. Bouwman, A.F.; Lee, D.S.; Asman, W.A.H.; Dentener, F.J.; Van der Hoek, K.W.; Olivier, J.G.J. A Global High-Resolution Emission Inventory for Ammonia; *Global Biogeochem. Cycles* **1997**, *51*, 561-587.
3. Van der Hoek, K.W. Estimating Ammonia Emission Factors in Europe: Summary of the Work of the UNECE Ammonia Expert Panel; *Atmos. Environ.* **1998**, *32*, 315-316.
4. Bouwman, A.F.; Van Drecht, G.; Van der Hoek, K.W. Global and Regional Surface Nitrogen Balances in Intensive Agricultural Production Systems for the Period 1970–2030; *Pedosphere* **2005**, *15*, 137-155.
5. Bouwman, A.F.; Van Drecht, G.; Van der Hoek, K.W. Surface N Balances and Reactive N Loss to the Environment from Global Intensive Agricultural Production Systems for the Period 1970–2030; *Pedosphere* **2005**, *48*, 767-779.
6. Parker, D.B.; Rhoades, M.B.; Schuster, G.L.; Koziel, J.A.; Perschbacher-Buser, Z.L. Odor Characterization at Open-Lot Beef Cattle Feedyards Using Triangular Forced-Choice Olfactometry; *Trans. ASAE* **2005**, *48*, 1527-1535.
7. Parker, D.B.; Pandrangi, S.; Greene, L.W.; Almas, L.K.; Cole, N.A.; Rhoades, A.B.; Koziel, J.A. Rate and Frequency of Urease Inhibitor Application for Minimizing Ammonia Emissions from Beef Cattle Feedyards; *Trans. ASAE* **2005**, *48*, 787-793.
8. Crook, B.; Robertson, J.F.; Glass, S.A.; Botheroyd, E.M.; Lacey, J.; Topping, M.D. Airborne Dust, Ammonia, Microorganisms, and Antigens in Pig Confinement Houses and the Respiratory Health of Exposed Farm Workers; *Am. Ind. Hyg. Assoc. J.* **1991**, *52*, 271-279.
9. Sakr, C.J.; Kreckmann, K.H.; Green, J.W.; Gillies, P.J.; Reynolds, J.L.; and Leonard, R.C. Cross-Sectional Study of Lipids and Liver Enzymes Related to a Serum Biomarker of Exposure (Ammonia Perfluorooctanoate or APFO) as Part of a General Health Survey in a Coherent of

- Occupational Exposed Workers; *J. Occup. Environ. Med.* **2007**, *49*, 1086-1096.
10. Schulze, E.D.; De Vries, W.; Hauhs, M.; Rosen, K.; Rasmussen, L.; Tamm, C.O.; Nilsson, J. Critical Loads for Nitrogen Deposition on Forest Ecosystems; *Water Air Soil Pollut.* **1989**, *48*, 451-456.
 11. Van Breemen, N.; Burrough, P.A.; Velthorst, E.J.; Van Dobben, H.F.; De Wit, T.; Ridder, T.B.; Reinjunders, H.F.R. Soil Acidification from Atmospheric Ammonium Sulfate in Forest Canopy Throughfall; *Nature* **1982**, *299*, 548-550.
 12. Krapac, I.G.; Dey, W.S.; Roy, W.R.; Smyth, C.A.; Storment, E.; Sargent, S.L.; Steele, J.D. Impacts of Swine Manure Pits on Groundwater Quality; *Environ. Pollut.* **2002**, *120*, 475-492.
 13. Pearson, J.; Stewart, G.R. The Deposition of Atmospheric Ammonia and Its Effects on Plants; *New Phytologist* **1993**, *25*, 283-305.
 14. Camargo, J.A.; Alonso, A. Ecological and Toxicological Effects of Inorganic Nitrogen Pollution in Aquatic Ecosystems: a Global Assessment; *Environ. Int.* **2006**, *32*, 831-849.
 15. Goetz, S.; Aneja, V.P.; Zhang, Y. Measurement, Analysis, and Modeling of Fine Particulate Matter in Eastern North Carolina; *J. Air & Waste Manage. Assoc.* **2008**, *58*, 1208-1214; doi: 10.3155/1047-3289.58.9.1208.
 16. Occhipint, C.; Aneja, V.P.; Showers, W.; Niyogi, D. Back-Trajectory Analysis and Source-Receptor Relationships: Particulate Matter and Nitrogen Isotopic Composition in Rainwater; *J. Air & Waste Manage. Assoc.* **2008**, *58*, 1215-1222; doi: 10.3155/1047-3289.58.9.1047.
 17. Wathes, C.M.; Demmers, T.G.M.; Xin, H. Ammonia Concentrations and Emissions in Livestock Production Facilities: Guidelines and Limits in the USA and UK. In *Proceedings of the American Society of Agricultural Engineers (ASAE) Annual International Meeting*; ASAE: St. Joseph, MI, 2003; Paper 034112.
 18. Aneja, V.P.; Arya, S.P.; Kim, D.-S.; Rumsey, I.C.; Arkinson, H.L.; Semunegus, H.; Bajwa, K.S.; Dickey, D.A.; Stefanski, L.A.; Todd, L.; Mottus, K.; Robarge, W.P.; Williams, C.M. Characterizing Ammonia Emissions from Swine Farms in Eastern North Carolina. Part 1: Conventional Lagoon and Spray Technology for Waste Treatment; *J. Air & Waste Manage. Assoc.* **2008**, *58*, 1130-1144; doi: 10.3155/1047-3289.58.9.1130.
 19. Bajawa, K.S.; Arya, S.P.; Aneja, V.P. Modeling Studies of Ammonia Dispersion and Dry Deposition at Some Hog Farms in North Carolina; *J. Air & Waste Manage. Assoc.* **2008**, *58*, 1198-1207; doi: 10.3155/1047-3289.58.9.1198.
 20. Faulkner, W.B.; Shaw, B.W. Review of Ammonia Emission Factors for United States Animal Agriculture; *Atmos. Environ.* **2008**, *42*, 6567-6574.
 21. Todd, R.W.; Cole, N.A.; Clark, N.; Flesch, T.K.; Harper, L.A.; Baek, B.H. Ammonia Emissions from a Beef Cattle Feedyard on the Southern High Plains; *Atmos. Environ.* **2008**, *42*, 6797-6805.
 22. Koziel, J.A.; Baek, B.-H.; Spinhirne, J.P.; Parker, D.B. Ambient Ammonia and Hydrogen Sulfide Concentrations at a Beef Cattle Feedlot in Texas. In *Proceedings of the American Society of Agricultural Engineers (ASAE) Annual International Meeting*; ASAE: St. Joseph, MI, 2004; Paper 044112.
 23. Venkatesan, S.; Sudahar, V.; Senthurpandian, V.K.; Murugesan, S. Urea Hydrolysis of Tea Soils as Influenced by Incubation Period, Soil pH, and Nitrification Inhibitor; *Comm. Soil Sci. Plant Anal.* **2007**, *38*, 2295-2307.
 24. Liu, G.D.; Li, Y.C.; Alva, A.K. Temperature Quotients of Ammonia Emission of Different Nitrogen Sources Applied to Four Agricultural Soils; *Soil Sci. Soc. Am. J.* **2007**, *71*, 1482-1489.
 25. Rochette, P.; Chantigny, M.H.; Angers, D.A.; Bertrand, N.; Côté, D. Ammonia Volatilization and Soil Nitrogen Dynamics following Fall Application of Big Slurry on Canola Crop Residues; *Can. J. Soil Sci.* **2001**, *81*, 515-523.
 26. Ansari, A.S.; Pandis, S.N. Response of Inorganic PM to Precursor Concentrations; *Environ. Sci. Technol.* **1998**, *32*, 2706-2714.
 27. 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*, 535-545.
 28. Denbigh, K. *The Principles of Chemical Equilibrium*, 4th ed.; Cambridge University: Cambridge, U.K., 1981.
 29. Kim, Y.P.; Seinfeld, J.H. Atmospheric Gas-Aerosol Equilibrium: III. Thermodynamics of Crustal Elements Ca²⁺, K⁺, and Mg²⁺; *Aerosol Sci. Technol.* **1995**, *22*, 93-110.
 30. Ferm, M. Atmospheric Ammonia and Ammonium Transport in Europe and Critical Loads—a Review; *Nutrient Cycl. Agroecosys.* **1998**, *51*, 5-17.
 31. Siva, K.B.; Aminuddin, H.; Husni, M.H.A.; Manas, A.R. Ammonia Volatilization from Urea as Affected by Humic Substances Derived from Palm Oil Mill Effluent (POME) and Tropical Peat; *Trop. Ag.* **2000**, *77*, 13-20.
 32. Pagans, E.; Font, X.; Sánchez, A. Adsorption, Absorption, and Biological Degradation of Ammonia in Different Biofilter Organic Media; *Biotechnol. Bioengineer.* **2007**, *97*, 515-525.
 33. Devlinny, J.S.; Deshusses, M.A.; Webster, T.S. *Biofiltration for Air Pollution Control*; Lewis: Boca Raton, FL, 1999.
 34. Schade, G.W.; Crutzen, P.J. Emission of Aliphatic Amines from Animal Husbandry and Their Reactions: Potential Source of N₂O and HCN; *J. Atmos. Chem.* **1995**, *22*, 319-346.
 35. Fitz, D.R.; Pisano, J.T.; Malkina, I.L.; Goorahoo, D.; Krauter, C.F. A Passive Flux Denuder for Evaluating Emissions of Ammonia at a Dairy Farm; *J. Air & Waste Manage. Assoc.* **2003**, *53*, 937-945.
 36. Peters, T.M.; Ott, D.; O'Shaughnessy, P.T. Comparison of the Grimm 1.108 and 1.109 Portable Aerosol Spectrometer to the TSI 3321 Aerodynamic Particle Sizer for Dry Particles; *Ann. Occup. Hygiene* **2006**, *50*, 843-850.
 37. Solorzano, L. Determination of Ammonia in Natural Waters by the Phenolhypochlorite Method; *Limnol. Oceanography* **1969**, *14*, 799-801.
 38. Parsons, T.R.; Maita, Y.; Lalli, G.M. *A Manual of Chemical and Biological Methods for Seawater Analysis*; Pergamon: Oxford, U.K., 1984.
 39. Lawrence, J. E.; Hornberger, G.M. Soil Moisture Variability across Climate Zones; *Geophys. Res. Lett.* **2007**, *34*, L20402.1-L20402.5.
 40. Yin, J.X.; Harrison, R.M. Pragmatic Mass Closure Study for PM_{1.0}, PM_{2.5} and PM₁₀ at Roadside, Urban Background and Rural Sites; *Atmos. Environ.* **2008**, *42*, 980-988.
 41. Auvermann, B.W. Lesson 42: Controlling Dust and Odor from Open Lots. In *Livestock and Poultry Environmental Stewardship (LPES) National Curriculum*. R. Koelsch, Ed.; Midwest Plan Service: Ames, IA, 2000.
 42. Upadhyay, J.; Auvermann, B.W.; Paila, A.N.; Hiranuma, N. Open-Path Transmissometry to Determining the Atmospheric Extinction Efficiency of Feedyard Dust; *Trans. ASABE* **2008**, *51*, 1433-1441.
 43. Hiranuma, N.; Brooks, S.D.; Auvermann, B.W.; Littleton, R. Using Environmental Scanning Electron Microscopy to Determine the Hygroscopic Properties of Agricultural Aerosols; *Atmos. Environ.* **2008**, *42*, 1983-1994.
 44. Malm, W.C.; Schichtel, B.A.; Pitchford, M.L.; Ashbaugh, L.L.; Eldred, R.A. Spatial and Monthly Trends in Speciated Fine Particle Concentration in the United States; *J. Geophys. Res.* **2004**, *109*, D03306.1-D03306.22.

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