

DOAS Measurement of Atmospheric Ammonia Emissions at a Dairy

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ABSTRACT

A new instrument for measurement of atmospheric ammonia based on short path ultraviolet spectroscopic absorption is now operational at the WSU Knott dairy farm near Pullman, WA. The instrument has a sensitivity of approximately 1 ppbv for NH_3 in an integration time of less than one minute with absolute accuracy approximately $\pm 20\%$. Concentration measurements have been made over the various settling lagoons, downwind from the lagoons, in the operations area of the dairy, and during the application of lagoon slurry to fields. An SF_6 tracer ratio technique has been used to obtain the NH_3 fluxes ($\pm 30\%$ accuracy) and to verify an atmospheric dispersion model. Determinations have been made in spring, summer and fall 2000. Preliminary summer ammonia fluxes ranged from 30 to $75 \mu\text{g}/\text{m}^2 \text{ s}$ from one of the settling lagoons for the 390 cow dairy.

INTRODUCTION

Ammonia emissions from livestock operations are a major environmental concern because 85% of ammonia emissions in the United States arise from agricultural sources (CENR, 2000). Noxious odor from ammonia and associated reduced sulfur compounds are an acute problem for dairy farmers making working conditions unpleasant and leading to lawsuits from neighbors (Riskowski et al., 1991). This is a particular problem where urbanization has encroached on traditional farmlands. However, ammonia emissions from dairies are more than just an odor problem. Agriculturally emitted ammonia is a major source of secondary particulate matter, $\text{PM}_{2.5}$, which is regulated under the new EPA National Ambient Air Quality Standard (ARS, 2000) as a human health hazard; the potential for additional air quality regulation accelerates the need for accurate estimates and mitigation of ammonia emissions (Meyer et al., 1999). The PM Measurements Workshop held in 1998 (EPA, 1998) recommends quantification of ammonia as an aerosol precursor measurement for $\text{PM}_{2.5}$ source attribution. "Current estimates of ammonia emissions to the atmosphere are characterized by a high degree of uncertainty" (CENR, 2000) since most estimates from livestock operations are calculated from the difference between known N imports and exports with unaccounted N assumed to be lost as ammonia. Because of the uncertainties in this indirect approach, it is very important to obtain better estimates of NH_3 emissions using more explicit, direct measurements of NH_3 emissions.

Livestock ammonia emissions arise from animal production units, from manure storage and lagoons, manure applied to land, urine, and manure deposition (Pain and Misslebrook, 1991). Manure collected and stored in lagoons undergoes natural decomposition and quickly consumes available oxygen, becomes anaerobic, and emits odorous gases, including ammonia. Lagoon management and alterations in livestock feed programs can significantly reduce ammonia release (Smits et al., 1997) through reducing the concentration of urea in urine or acidifying the lagoon slurry. Additional management practices can include lagoon mixing or aeration to prevent the anaerobic conditions that result in the formation of odorous compounds (Westerman and Zhang, 1997). Published work on

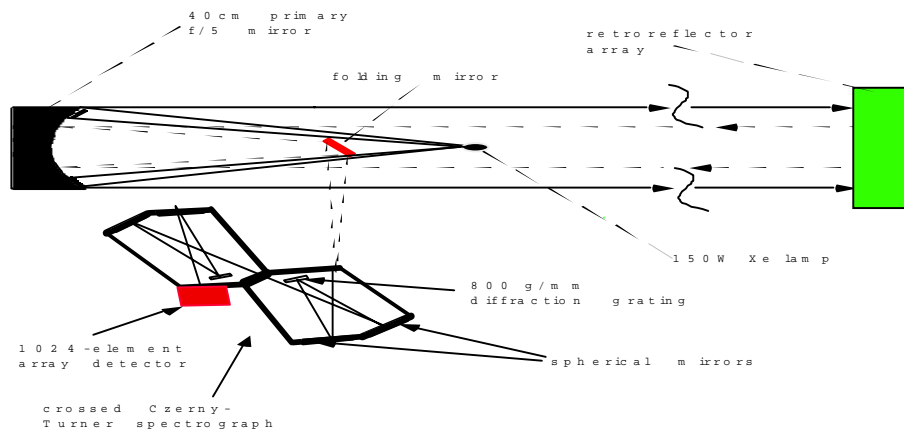
ammonia emissions is based on a small number of short-term measurements that involve considerable uncertainty (Demmers et al., 1999), and are mostly concentrated in Europe where farming practices differ significantly from the U.S. Consequently it is difficult to evaluate the impact of management practices on ammonia emissions in this country.

In this paper we report preliminary concentration and flux results from the primary sewage settling lagoon and concentration results from the application of sewage slurry to grass fields.

AMMONIA INSTRUMENT

Accurate measurement of ammonia is not easy because ammonia adheres strongly to inlet lines and collection surfaces rendering in situ methods unreliable (Williams, 1992). Fehsenfeld (1995) has recommended that direct spectroscopic detection of NH_3 without the intervention of a collecting medium would provide continuous, unequivocal, and calibrated measurements. We have developed, and now have extensive experience with, an open path measurement system which utilizes well tested spectroscopic techniques developed by the authors and others (e.g. Mount and Harder, 1995; Galle et al., 2000). This method has been used by our group extensively for over 10 years in difficult field conditions and has proven accurate and reliable (e.g. Harder et al., 1997; Plane and Smith, 1994).

We are measuring ammonia at the WSU dairy farm by short path spectroscopic absorption in the mid-ultraviolet spectral region. This method is particularly clean, involving operation in the open air with no walls or inlets for ammonia to adhere. In addition, the method is self-calibrating, being dependent only on the precision of the measurement, the absolute cross section of the gas being measured, and easily determined geometric factors. Ammonia is measured in the ultraviolet bands near 210nm wavelength with a lower sensitivity limit of several parts per billion in an integration time of several seconds to an accuracy of approximately $\pm 20\%$. The system we have developed and tested is conceptually simple, consisting of 1) a bright and spectrally broad ultraviolet light (UV) source, 2) a telescope to beam the UV light into the atmosphere, 3) a mirror system to reflect the light back towards the light source, 4) a receiver telescope to focus the light spectrally absorbed by the atmosphere onto a dispersing spectrograph, 5) a multi-element multiplexing digital detector, and 6) a data analysis system. Figure 1 shows a basic schematic of the system. The ultraviolet light source is a xenon high pressure emission lamp. The telescope is a 40 cm diameter parabolic mirror operated in Newtonian configuration. The mirror reflector system consists of three large (127 mm) retroreflector arrays, which turn the light beam around on itself. The beam absorbed in the atmosphere is focused onto a custom-made double spectrograph for spectral analysis. The detector for the experiment is a state of the art homebuilt Reticon silicon photodiode array



A m m o n i a M e a s u r e m e n t S y s t e m

Figure 1. A schematic of the WSU ammonia measurement system. Arrows indicate the direction of travel of light beams, as do solid (out from telescope) and dashed (in to telescope) lines. The retro array is positioned so it displaces the light to the system center line, thus illuminating a dark section of the primary mirror for reflection into the spectrograph by the folding (red) mirror.

system which makes this instrument superior to normal scanning spectrometer systems [Mount et al., 1992]; the entire spectrum is measured simultaneously. The detector and spectrograph have been used extensively in the field and perform very well (e.g. Hofmann et al, 1995).

An extensive algorithm have been developed for analysis of the photodiode array data. Variants of the software system has been used in the field since 1986 utilizing a nonlinear least squares program that solves the Beer-Lambert absorption law [Strong, 1952]. In its simplest form, this law states

$$\ln [I(\lambda) / I_0(\lambda)] = -L \sum \sigma_i (\lambda) N_i \quad (1)$$

where:

λ = wavelength (nm)

$I(\lambda)$ = light intensity in the presence of absorbers (counts)

$I_0(\lambda)$ = light intensity without absorbers (counts)

L = optical path length (cm)

$\sigma_i (\lambda)$ = absorption cross section of the i^{th} absorber (cm^2) [Rayleigh scattering, NH_3 , NO , SO_2]

N_i = abundance of the i^{th} absorber (molecules cm^{-3}).

The effect of other absorbers in this spectral region (e.g. NO , SO_2) is recognized, but should not be a problem in this work due to low abundance. In any case, interfering molecular spectra are measured and removed from the spectrum. Count rates and absorptions for the ammonia experiment for a 50 m path (typical of a lagoon) show signal-to-noise ratio in several seconds of over 1000:1. This is more than adequate to make an accurate measurement.

Gas absorption cross sections of NH_3 , SO_2 , and NO (the three molecules that absorb with a structured spectrum near 210 nm in the atmosphere) were carefully measured in the laboratory with the field instrument. There are a number of papers on ammonia photoabsorption cross sections (e.g. Mellquist and Rosen, 1996) and our results agree with the published values within about 30%, well within the measurement errors of the various experiments, thus insuring an accurate calibration to produce a good ammonia value.

The instrument is operated from a small trailer with the reflective mirror system placed some meters distant depending on spatial averaging desired and anticipated level of sensitivity required. Set up time is about one hour and requires mirror positioning and then accurate alignment to direct the light into the spectrograph. Spectra can be taken as fast as every few seconds, or averaged in the computer over a longer time period (typically 5 minutes corresponding to the integration time of our meteorological system). Power requirements for the entire system are approximately 1 kW. When operating without house power, a portable generator is used. Instrument specification are summarized in Table 1.

Table 1. Summary of Ammonia Instrument Characteristics

- integration time for ammonia measurement: approximately 1 second
- typical averaging time for reporting data: 5 minutes
- path length: few meters to 750m
- sensitivity limit: 1 ppbv
- error in ammonia concentration: $\pm 20\%$
- integration time for tracer release: 30 min.

- ammonia emissions sensitivity limit: $5\mu\text{g}/\text{m}^2/\text{sec}$
- error in ammonia fluxes: $\pm 30\%$

An uncalibrated experiment was conducted in the field to verify measurement of ammonia. Measurements were made in a nominally ammonia free area and then liquid ammonia was volatilized over the short path. Ratios of the two spectra produced the clear signature of ammonia in the spectrum.

Meteorological measurements are made at the dairy with a standard portable Campbell weather station. Wind speed and direction are measured at 3m, temperature and relative humidity at 2m and temperature gradient at 1 and 3 m.

CONVERSION OF CONCENTRATIONS TO EMISSION FLUXES

Because the basic measurement made is ammonia concentration, we must convert to emission fluxes. The basic method utilized is a gas tracer to simulate ammonia and determine the ammonia emission rate from a tracer ratio calculation:

$$Q_p = Q_t (CWI_p/CWI_t) \quad (2)$$

where Q_t is the tracer release rate, and CWI_p and CWI_t are measured ammonia and tracer crosswind integrated concentrations co-located at the downwind site (with subtraction of upwind, background ammonia and tracer concentrations). We have found that the ratio of crosswind integrated concentrations is more robust compared to use of single point concentration data since using the crosswind integrated concentrations reduces errors associated with differences in the exact source configurations for the pollutant and tracer releases. We have employed this method to measure emissions of methane from a wide variety of sources in the natural gas industry (Lamb et al., 1995), fluxes of methane from landfills (Czepiel et al., 1996), volatile organic compound emissions from a wastewater treatment basin (Howard et al., 1992), PM_{10} emissions from roadways (Mitra et al., 1995; Kantamaneni et al., 1996), and isoprene emissions from an oak tree grove (Lamb et al., 1986). The tracer ratio method has the advantage that it eliminates the need for detailed meteorological measurements and the requirement to invoke any kind of diffusion model. It also has the advantage that it can be applied individually to relatively small discrete sources or to a group of sources to provide a total, integrated source emission measurement. It is assumed that the tracer release simulates the source and that the pollutant and tracer are transported in the same way in the atmosphere. The first requirement can be addressed by releasing tracer gas from a number of points distributed throughout the source area and by sampling far enough downwind to insure well-mixed tracer and pollutant plumes. The second requirement is fulfilled since atmospheric transport is dominated by turbulent diffusion and advection and does not depend upon the molecular properties of either the tracer or pollutant. In our applications, we employ sulfur hexafluoride (SF_6) as the tracer gas. SF_6 has been used as an ideal atmospheric tracer for more than 30 years in a wide variety of atmospheric transport studies ranging in scale from indoor air quality tests (Lamb et al., 1985) to long range transport over distances as large as 150 km (Lamb et al., 1990).

WSU DAIRY CENTER

The WSU dairy operation is typical of most Pacific Northwest dairies in that cows are maintained on concrete slabs with access to covered free-stall barns. Manure is scraped from the concrete slabs onto grates from which the manure is flushed into a manure separator with the liquid waste stream flowing into lagoons. The growing heifers are kept in a heifer barn with a concrete exercise area located about 50 yards away from the lactating cows, and the dry cows are located in an open shed and have access to a dry lot. Figure 2 shows a scale schematic of the dairy farm. The WSU dairy houses 190 Holstein cows and 200 growing replacement heifers. The average annual milk production of the herd is currently 11,100 kg/cow. The herd diet contains 20.6% CP, i.e., 3.3% N. Total

animal imports to the dairy equal an estimated 59,000 kg. The exports of N in milk and animals from the dairy equal approximately 19,000 kg. Thus, the net annual accumulation of N at the Dairy Center is about 40,500 kg. That amount of nitrogen is removed either by the solids separator or from the storage lagoons where the N either evaporates as ammonia or is applied to fields for nitrogen fertilization of crops.

Figure 2. Schematic of the dairy. The lagoons hold about 45,000 m³ of slurry. Most of the flux work as been downwind of lagoon 2. Wind direction is typically from the upper left of the figure diagonally across. Scale is approximately 30m per cm.

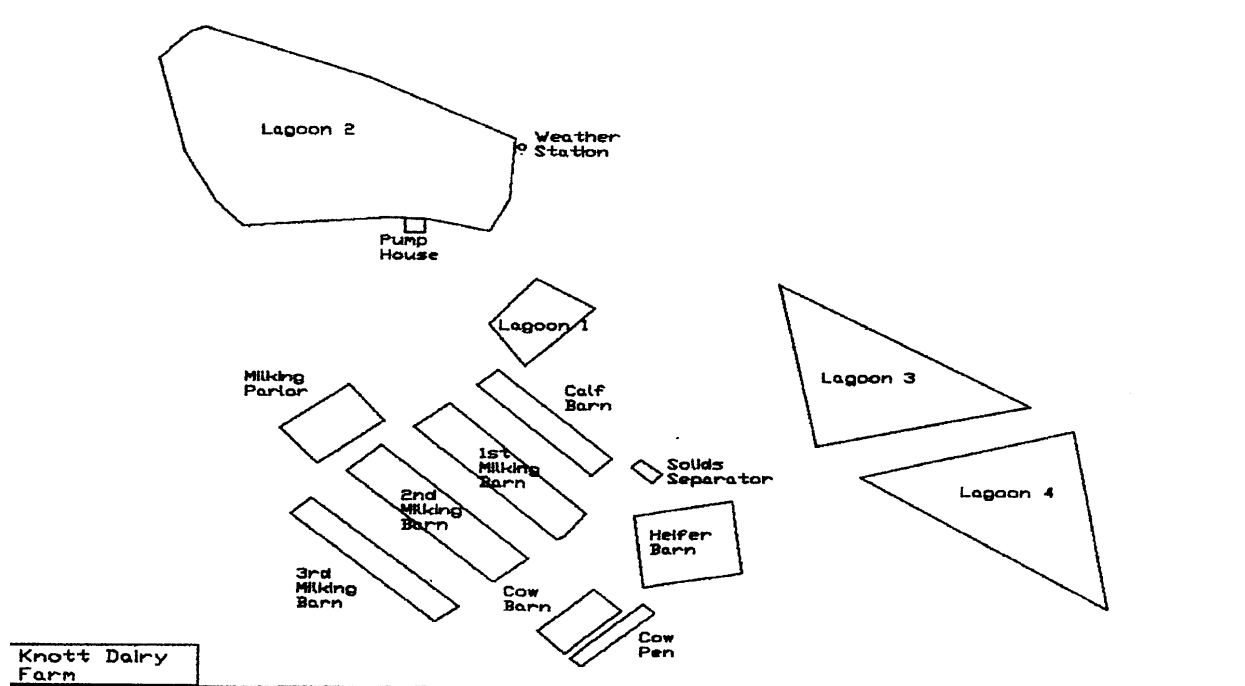


Figure 3 below shows a photograph of the dairy operations area (with main settling lagoon 2 behind the copse of trees). Figure 4 below shows lagoon 2 where most of the lagoon measurements were made.



Figure 3. Overall view of the WSU dairy. Lagoon 2 is just beyond the copse of trees. Lagoon 3 is on the right. The barns in the picture house the dairy herd.



Figure 4. Lagoon 2 with the NH₃ measurement system downwind in center right.

We have begun an active program to monitor the water in the slurry lagoons for dissolved ammonia as well as other nitrogen compounds on a biweekly basis. Clearly the chemistry of the lagoon has a large impact on ammonia emitted into the air. Anaerobic conditions predominate, but with aeration of the lagoon, those conditions will change. In order to close the nitrogen balance and define the effects of aeration on ammonia emissions, an understanding of the fate of nitrogen in a lagoon system is required (Westerman and Zhang, 1997). These data are also a critical part of developing a complete understanding of the ammonia flux data that are collected as part of the atmospheric sampling campaign.

Based on current lagoon operation, the low solids pond acts as a facultative treatment lagoon (aerobic surface water and anaerobic subsurface) and, as such, is likely the major contributor of ammonia and other odor causing compounds. Odor causing compounds in lagoon systems are directly related to operating conditions (organic carbon and nitrogen loading, detention time, degree of mixing, temperature, pH, oxidation-reduction potential, etc.). Lagoon monitoring includes quantification of influent and effluent flow and selected constituent concentrations as well as water column and sludge monitoring within the pond. The data resulting from this monitoring effort define the ammonia production potential of the lagoon and afford a means of completing an ammonia balance when combined with the ammonia flux measurements.

AMMONIA CONCENTRATIONS / PRELIMINARY AMMONIA FLUX DETERMINATIONS

There are three main sources of ammonia at the WSU dairy: the dairy barn-feeding area, the separator-solids pool, and the three large primary lagoons. The waste from the dairy herd in the barn areas is pushed once per day into a drain that is continuously flushed with lagoon water and sent to a separator that removes gross solids. The liquid slurry is transported by gravity to a small, high solids lagoon for further solids separation via gravity sedimentation. The overflow from the high solids lagoon flows by gravity to a low solids lagoon. The low solids lagoon is pumped out several times per year to two large holding ponds (10M gallons). The low solids lagoon 2 acts as the primary manure treatment unit and as such, is expected to be the major contributor of ammonia from anaerobic biological activity. Consequently atmospheric measurements regarding the lagoon system is focused at the low solids lagoon with additional measurements taken around the barns, solids separator, the high solids lagoon and lagoons 3 and 4. The dairy slurry lagoons are well positioned for measurement – easy to get to and located such that the prevailing winds (WSW) do not blow across the operational area of the dairy.

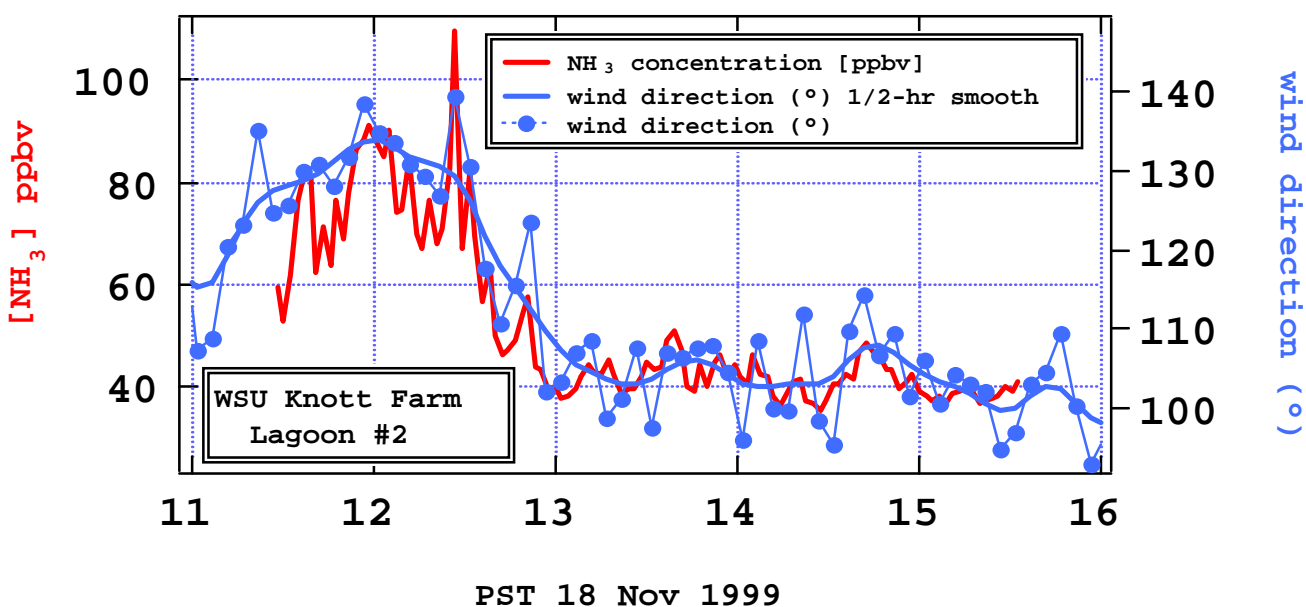
Ammonia concentrations are obtained with the open path system, while tracer concentrations are obtained from portable syringe samplers (Krasnec et al., 1984) deployed along the line of sight of the NH_3 system as described above and shown in the figure below.

Figure 5. The line of SF_6 syringe samplers in operation along a 70m absorption path. Lagoon #2 is upwind to the left of the picture approximately 100m.



SF₆ measurements are made during sequential 30-min averaging periods for 5 hours at each syringe station. Ammonia data is taken on 5-minute centers and averaged to 30 minutes for calibration. The syringes are returned to the WSU laboratory for analysis immediately following each experiment. The analyses are conducted using commercial electron capture gas chromatographs (HP 5890) calibrated with certified commercial SF₆/air standards (Scott-Marrin, Inc., ±5% accuracy). The measurement system for lagoon #2 is located about 175m downwind of the lagoon to allow sufficient mixing of the tracer and ammonia plumes. SF₆ was released through a line source deployed along the entire upwind edge of the lagoon over a length of 100m. The line source is designed to provide a uniform, steady release of tracer gas from capillary restrictors located every 4m along the line (Finn et al., 1996).

Figure 6 shows typical ammonia concentration measurements directly over lagoon #2 in the



winter averaged to 5-minute time centers.

Figure 6. Ammonia concentrations made on 18 November 1999 directly over lagoon #2. These values increase by about a factor of 50 in summer. Note the strong correlation of ammonia with wind direction. This is expected since a SW wind blows over the long direction of the lagoon; an E wind blows over the shortest section, thus varying the fetch across the lagoon and increasing or decreasing observed ammonia.

We have made concentration measurements since fall 1999 with regular measurements in summer 2000. Most measurements have been made downwind of lagoon #2 since downwind measurements are required to insure adequate mixing of the calibration tracer gas with the ambient air flow when we perform calibrations. Figure 7 below shows a typical run with the instrument about 70m downwind from lagoon 2. Variations with wind direction are expected.

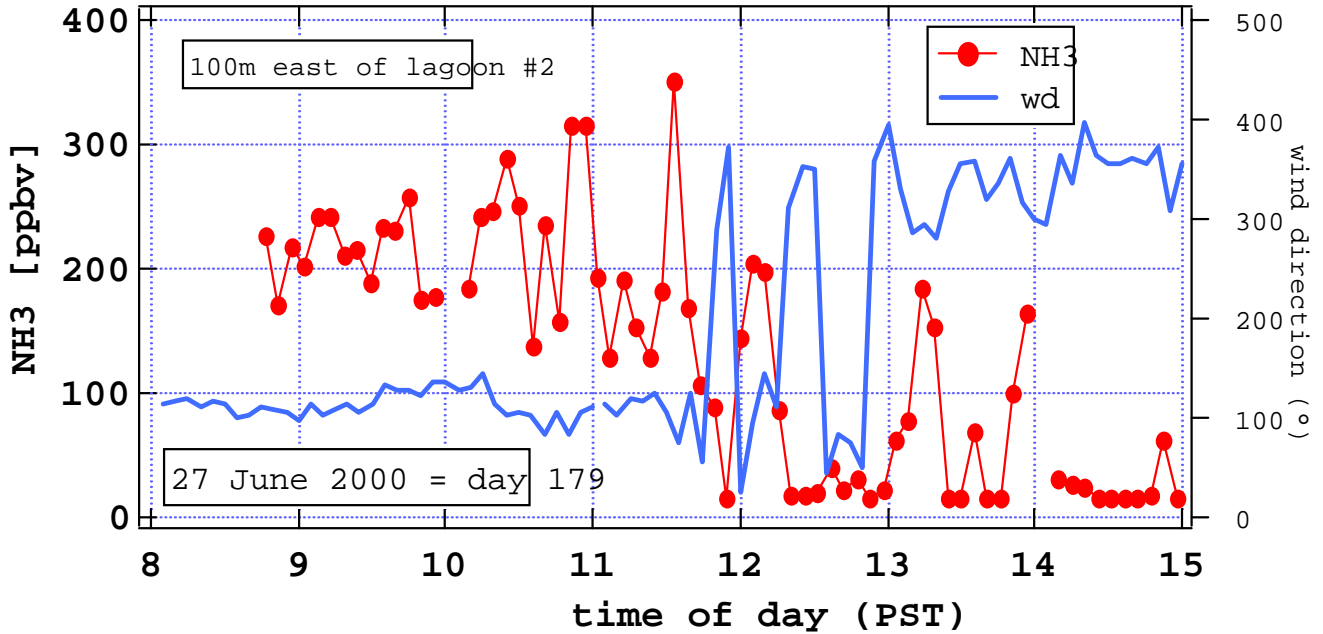


Figure 7. Ammonia concentration measurements made downwind from lagoon #2 on 27 June 2000.

Figure 8 shows ammonia concentrations from sprinkler application of slurry to a field (95 m³/hr). These measurements began across the field prior to application and continued right on through the rainbird spray and on as the gun was dragged across the field at 25m/hour. There is a surface temperature inversion at night showing a large increase in ammonia concentrations and wind-dependent changes in concentration as the wind came up during the night and morning hours. Variations in ammonia concentration are directly traceable to wind direction and speed changes. We did not make an SF₆ release on this day, so emission fluxes are not available. After 36hr, ammonia has still not returned to negligible preapplication concentrations.

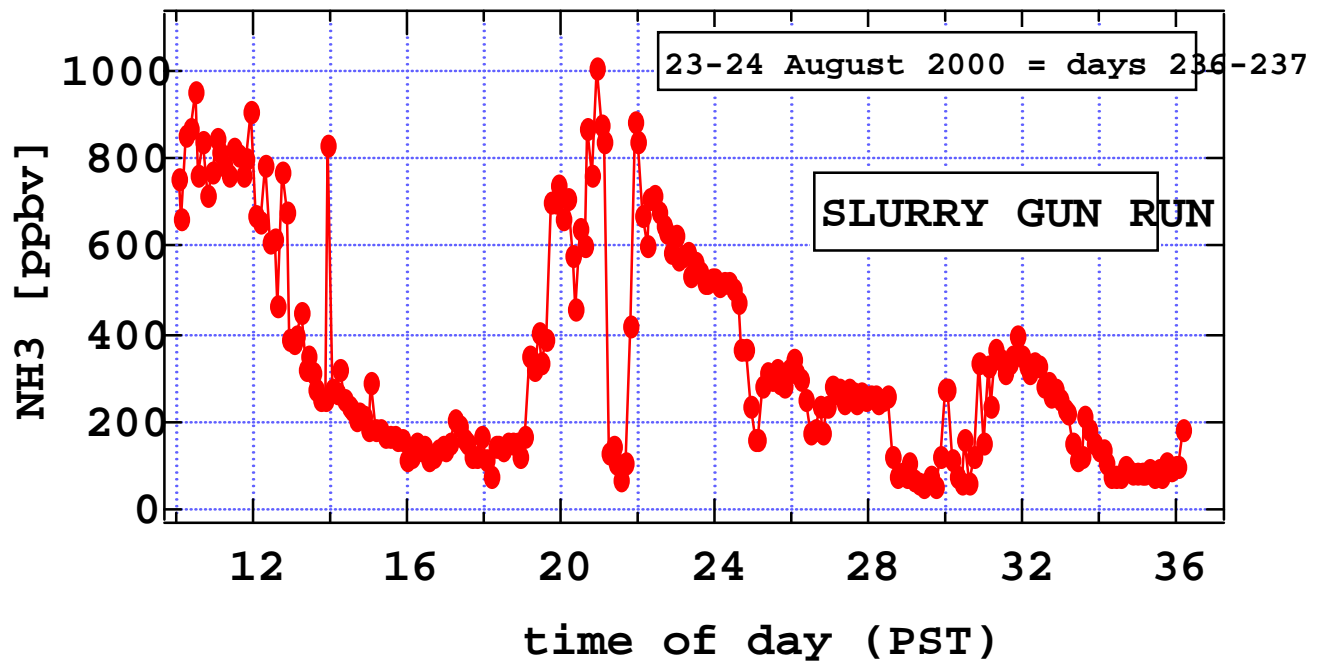


Figure 8. Measurements of slurry application on 23-24 August 2000. The slurry gun was in the instrument field of view when the experiment began and was pulled through the instrument field of view at 25m/hour, exiting the FOV about 1230h. Note the large night inversion.

Considering the dairy ammonia emissions as a whole, if 20% of the N in the animal wastes is lost as ammonia (see above), it represents an annual contribution of about 8,100kg of ammonia into the atmosphere. A recent estimate (Bouwman et al., 1997) gives a value as high as 36% of the N wastes will convert to ammonia for an annual contribution of 14,600kg. Our preliminary flux measurements yielded approximately $30\mu\text{g}/\text{m}^2 \text{ s}$ at 11°C and $75\mu\text{g}/\text{m}^2 \text{ s}$ at 22°C air temperature over lagoon 2 in July 2000 during the morning and early afternoon. We have not converted this to an annual average N since we do not have calibrated tracer experiments extending all year. Rather, since it is not practicable to run sulfur hexafluoride syringe calibrations simultaneously with all of the ammonia determinations, we are developing methods based upon upwind/downwind concentration measurements (mass balance methods) to obtain estimates for comparison to the tracer results and verification of the plume model.

To interpret the upwind/downwind concentration measurements, we use a simple, but realistic, Gaussian plume model and back-calculate ammonia fluxes from the observed concentrations. To simulate lagoon emissions, a dense array of individual point sources at 1 m spacing are employed and the plume from each point source moved downwind to the receptor location is superimposed to yield the total concentration at each downwind receptor. Diffusion coefficients are determined from available turbulence measurements from the met station at the lagoon. We adjust the point source emission rates until agreement is achieved with the concentrations measured downwind with the ammonia instrument. The model is also used with a line source model to simulate the SF_6 release and provide a direct calibration of downwind ammonia during syringe measurements. This gives much confidence in the use of the model for times at which the tracer ratio method cannot be used. Thus, we use the tracer data to validate the diffusion model. In turn, the validated model will allow us to estimate ammonia fluxes during periods when only the ammonia instrument is operating (without tracer ratio measurements) and thus it provides a way to extend the period of time when we measure ammonia emissions.

Figure 9 below shows an airplane view of slurry lagoon #2. The dense points are the source areas, the grey solid line on the right shows the receptor region. Wind typically blows from the west (LHS of figure) across the lagoon and to the instrument. A wind vane is shown above the lagoon representation. At the receptor area, color and receptor size is used to show the concentration of ammonia. In this case, we have a west wind (270°) blowing at 4.7 m/s across the lagoon. The lagoon sources emit, in this case, at $30\mu\text{g}/\text{m}^2 \text{ s}$ and each point is 1m apart. The Gaussian plume model is run using the real met data from the lagoon meteorological station on 5-minute centers for the entire day. As wind shifts, the receptor area is more or less covered with the ammonia plume and so the concentrations change, sometimes radically, with wind direction and speed.

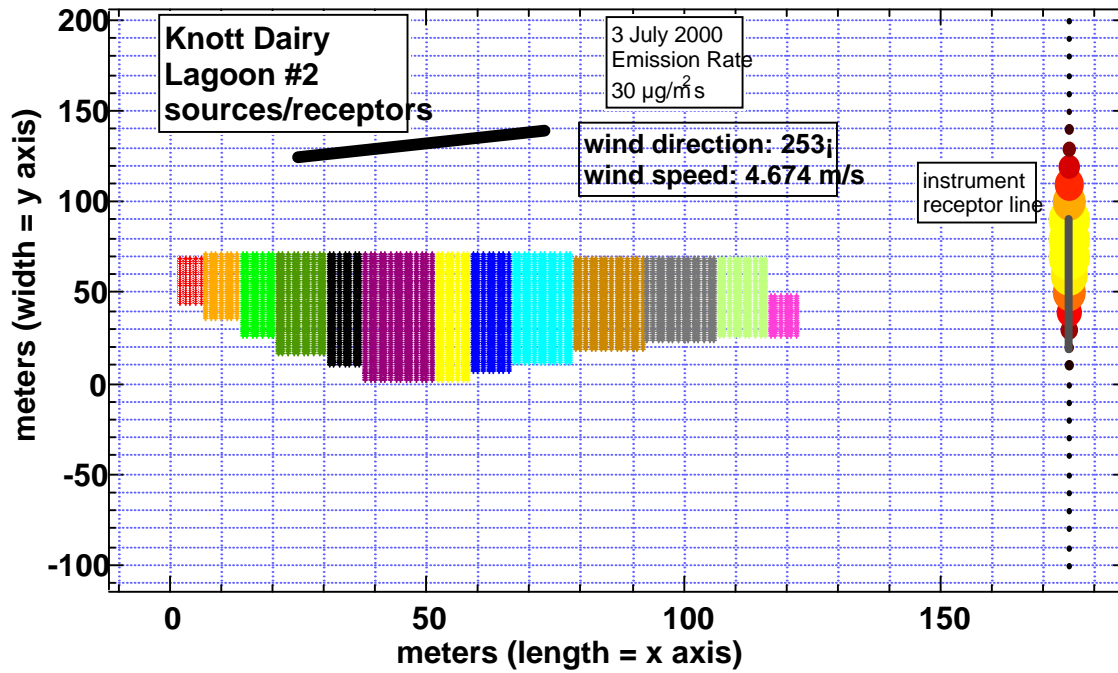


Figure 9. An airplane view of lagoon #2 and the instrument receptor area (solid vertical line). The color and size of the modeled receptor points (spaced 10m) indicate the concentration of ammonia at that point. The lagoon matrix is 1m x 1m. A wind vane (solid black) shows wind direction.

Figure 10 below shows the comparison of the modeling run with the measured concentrations for 5 July 2000, the same day shown in Figure 9. Although agreement is not exact, there is relatively close correlation of peaks and valleys which are generally related to changes in wind direction and speed.

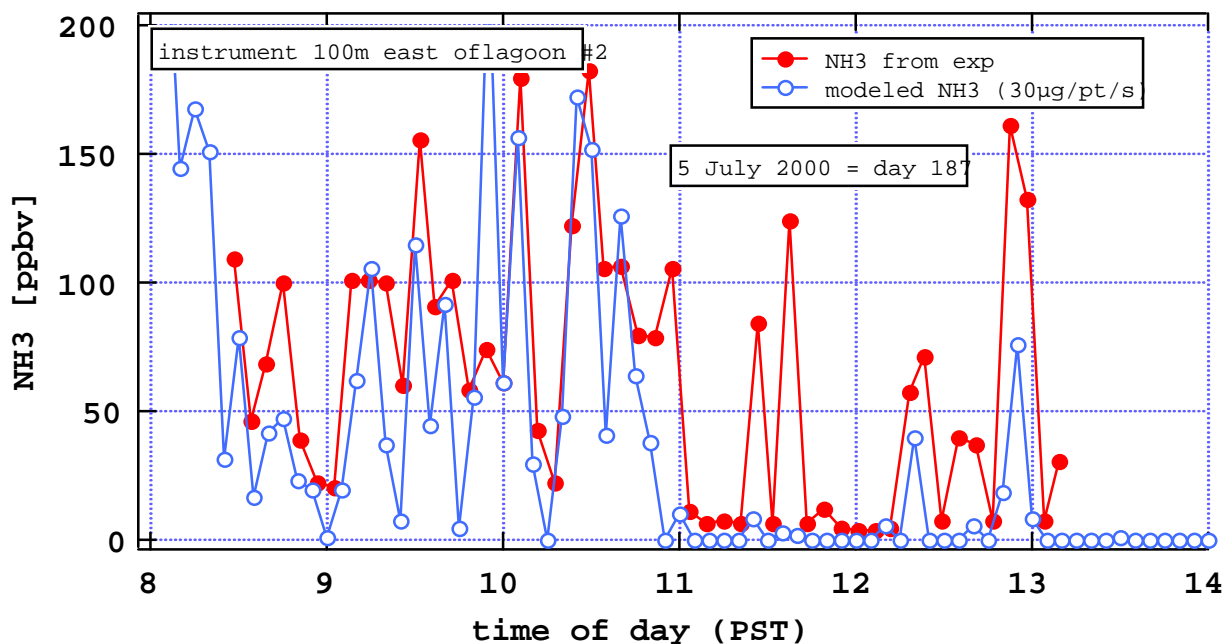


Figure 10. Concentration data from the ammonia instrument located downwind of lagoon #2 and modeled data for the same day using real met data and a Gaussian plume model. The large variations are due to changing wind direction and turbulence, with the modeled concentrations following the observed concentrations fairly well.

CONCLUSIONS

We have described a new instrument to make ammonia concentrations at reasonable sensitivity in a short time period, and have shown initial data from use of that instrument at the WSU operating dairy near Pullman, WA. Concentration measurements range from 10s of parts per billion over the slurry lagoons in the winter to parts per million levels in the summer. Concentrations measured 60 m downwind range from 10s of ppbv to hundreds of ppbv. Flux measurements made using a tracer ratio method show summer emissions above the primary slurry lagoon to be in the range 30-75 $\mu\text{g}/\text{m}^2 \text{ s}$ between 11 and 22°C. A plume model has been developed to back calculate fluxes from NH_3 concentrations. This model has been validated with a SF_6 tracer release with calibrated line emissions and measured concentrations at the ammonia instrument.

This work has been supported by Washington State University

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keywords: ammonia emissions, dairy farm, spectroscopic instrumentation