Comparison of Ambient Ammonia Measurement Techniques from Dairy Area Sources

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Comparison of Ambient Ammonia Measurement Techniques from Dairy Area Sources

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Abstract. Previous studies of ag-related NH$_3$ concentrations and/or emissions have used a variety of techniques, with very few studies offering adequate instrumental comparisons. In the fall of 2007, NH$_3$ concentrations/emissions were monitored for a one week period at a waste treatment lagoon on a 6000-cow dairy in Idaho using five separate methodologies. Up to twenty-five Ogawa passive samplers were dispersed around the perimeter of the lagoon, with a concentrated bank of samplers arrayed along the predicted downwind side of the facility. A URG acid/base gas denuder system, assembled with three series denuders configured for NH$_3$ collection, was collocated at a single sampling site with one of the passive samplers. The collected samples from the passive samplers
and the denuder tubes were quantified via ion chromatography at Utah State University. Two separated UV-Sentry open-path ultra violet differential optical absorption spectrometers (UV-DOAS) were used to measure the integrated NH$_3$ concentrations along an approximately 200 m pathlength on both the up and downwind sides of the lagoon. Two infrared Fourier Transform Spectrometers (FTS) were also used to quantify ambient NH$_3$ along the same downwind pathlength. Finally, a small, floating wind tunnel system, coupled with a Thermo Fisher Model 17C chemiluminescence NH$_3$ monitor, was used to measure direct NH$_3$ emissions from the surface of the lagoon. In 2008, NH$_3$ measurements were made at a 950-milking cow dairy in central California. Two FTS systems were employed upwind and downwind of the whole facility, while numerous passive samplers were placed throughout the dairy. Quantification of all ambient concentrations have been completed and the measurements will be used in conjunction with inverse modeling techniques (both LaGrangian and Eularian) to estimate lagoon and dairy-wide NH$_3$ emissions.

**Keywords.** dairy, ammonia, emission rate, lagoon, measurement techniques
Introduction

Ammonia (NH₃) is the major basic species and one of the most abundant nitrogen-containing compounds in the atmosphere (Seinfeld and Pandis, 2006). This compound plays an important role in atmospheric chemistry due to its acid neutralizing capacity and role in the formation of secondary particulate matter. In addition, NH₃ is very depositional and can have a significant influence on the terrestrial environment as well. Direct human effects include an unpleasant odor and, in high enough concentration, irritation to the respiratory tract and other soft tissues in the body. Similar effects have been observed in agricultural livestock, including reduced production and animal death at high (10’s of ppm) concentration (Holland et al, 2002). NH₃ originates from several different sources, the largest of which is the agricultural industry, which contributes an estimated 85% of the NH₃ emissions in the United States (CENR, 2000).

Multiple techniques have historically been used to measure agricultural related NH₃ concentrations, yet few instrumental comparisons have been made. In this study, near source ambient measurements were made at two large agricultural facilities and compared. Measurement instruments included Owaga passive samplers, an annular denuder system, Fourier transform infrared spectroscopy (FTIR) systems, an ultra violet differential optical absorption spectroscopy (UV-DOAS) system, and a wind tunnel in combination with a chemiluminesence NH₃ monitor. Most of these measurements were subsequently used in conjunction with two EPA approved modeling techniques, ISCST3 and AERMOD, to estimate dairy lagoon and facility emission rates. Additionally, a backward Lagrangian stochastic model (WindTrax) was used to estimate emissions based on the DOAS system.

Methodology

Data were acquired during two field campaigns. The first study was at a 6000-head freestall dairy in south-central Idaho and took place in early October 2007. The second study took place at an 1800-head freestall dairy in central California in June 2008. All of the measurement systems were employed during the Idaho study, but only the FTIR and passive systems were employed at the California study.

Instrumentation

Ogawa passive samplers (Ogawa USA, Inc., Pompano Beach, Florida) were used to obtain time-averaged concentrations of NH₃. These samplers are constructed of a Teflon cylinder with two open, unconnected ends. Each end is capped with a perforated end cap that acts to hold a sample pad between two stainless steel screens. Samples are collected as air diffuses through the holes in the end cap and screen and any NH₃ is captured on the sample pad (citric acid coated pads are used for NH₃ collection). Following sample collection, the sample pads are eluted using de-ionized water to transfer the NH₃, in the form of NH₄⁺, into solution, and the solution is analyzed using ion chromatography (IC).

The annular denuder system (URG Model 3000C) is designed to dynamically collect particles and gaseous species simultaneously. As air is pulled through the sampler, a series of denuder tubes followed by a filter pack, the gaseous species migrate to the coated denuder walls. In this case, a coating solution consisting of citric acid, methanol, and glycerol was used for the collection of NH₃. Finally, particles contained in the sample air become entrapped on a filter. The URG denuder is modular to allow for different setups according to sampling needs. During sampling, two tubes were used to collect samples, differing only during the longer, nighttime run, when three tubes were placed in series to avoid any breakthrough. After the samples were
collected, the coating was rinsed off using deionized water and collected for analysis. As with the passive samplers, analysis of NH$_4^+$ was performed using IC.

The UV-DOAS (UV sentry, Cerex, GA) was used to determine path integrated concentrations. The DOAS contains a light source, a Xenon lamp, that sends a broadband ultra-violet signal (NH$_3$ gas absorbs light in the region of 200-350 nm) across the sample pathlength to a receiver placed at the other end (approximately 230 m). The collected signal is transmitted via a fiber optic device to a detection system where it is multiplied and quantified. System configuration is more fully outlined in de Haro Marti et al. (2007).

Integrated path concentrations were also determined using three different FTIR spectrometers. In one instrument, owned by the Space Dynamics Lab (SDL) associated with Utah State University, utilizes an active infrared source to create a beam which is transmitted through a Bomem double pendulum interferometer and other transmitting optics. The modified beam then passes through the sample air and is returned by a retroreflector. The beam then passes through the receiving optics to a sterling cycle cooled MCT detector, producing an interferogram. The interferogram is then manipulated and fit to a spectral library to determine the species present and the concentration of those species. The second FTIR system was borrowed from the University of Idaho (UofI) and differs somewhat from the SDL spectrometer in that it has a Bomem Michelson interferometer with a liquid nitrogen cooled detector (Going et al., 2008). The third system was a system owned and operated by ARS.

The wind tunnel system was an open bottomed, stainless steel enclosure placed directly over the emitting source (the wastewater lagoon) and tethered in place while ambient air was drawn through a filter and then through the tunnel to mix with and transport the emissions away from the emitting surface. This combined stream was then transported to the analytical system, a Thermo Fisher Model 17C chemiluminescence NH$_3$ monitor, via Teflon tubing. This system is more fully described by Sheffield and Louks (2006).

Meteorological data used in data analysis and modeling were collected using a Davis Weather Station Vantage Pro Plus. In addition, Hobo sensors were used to collect vertical temperature data to be used in determining atmospheric stability classes. Wind direction, velocity, and temperature data utilized in combination with the measurements made by the UV-DOAS system were obtained with a three dimensional (3-D) anemometer (R.M. Young).

**Sampling configuration**

At the first (Idaho) location, a large (approximately 24.2 acre) wastewater lagoon was the focus of the measurements. Twenty-five passive samplers, with two being used for duplicate measurements, were deployed surrounding the lagoon. A URS denuder system was collocated at one of the passive sampler locations. In addition, two DOAS systems were located one each on the east and west sides of the lagoon to collect integrated measurements along an approximately 250 meter pathlength, with one of each system presumably upwind (background) and downwind of the source. Two FTIR spectrometers (the SDL and U of I instruments) were also placed on the east bank to collect measurements along the assumed predominately downwind pathlength. The parallel FTIR systems were setup as an intercomparison between the two similar systems. Additional measurements were made with a floating wind tunnel system to obtain direct NH$_3$ emissions from the lagoon. A schematic of the general sampling setup is shown in Figure 1. In this location nine daytime sampling periods of about three to five hours length and one 14 hour nighttime period were completed.
During the second test (California), a total of thirteen twelve hour sampling runs were conducted. Sampling periods were roughly from midnight to noon or noon to midnight. Unlike the Idaho study where the focus was on the lagoon emissions, the California measurements attempted to quantify whole-facility NH$_3$ concentrations and emissions. The dairy contained a total of 1800 cattle housed in a number of pens separated by age and role. The distribution of cattle was: 950 milk producers, 100 dry cows, 800 heifers evenly distributed between the age of two years and 1 day, and 30 bulls. The waste produced by these cattle was flushed into an approximately 1500 m$^2$ solid separator. Water seeping out of the solids then drained into a 5800 m$^2$ wastewater lagoon. Figure 2 contains a schematic of this dairy sampling set up. To quantify emissions at this location, 23 Owaga samplers were deployed throughout the overall dairy facility. Additionally, two FTIR spectrometers were employed. One instrument, the SDL spectrometer, on the presumed downwind (south) side operating with multiple reflectors to collect data over different sampling paths, and another, operated by ARS-Ames, Dr. Richard Pfeiffer, on the upwind (north) side of the dairy. As described and can be derived from Figure 2, the downwind FTIR system was located near the Air Quality base trailer (AQT in the figure) such that the FTIR system turret could rotate and align with a series of reflectors to the west and east across the base of the facility.
Modeling Techniques

Included among the U. S. EPA approved models listed in Appendix W of 40 CFR Part 51 (U. S. EPA, 1998) are the Industrial Source Complex Short-Term Model (ISCST3) and the American Meteorological Society/Environmental Protection Agency Regulatory Model (AERMOD). In November 2005, AERMOD was recommended for all regulatory applications (U. S. EPA, 1995; U. S. EPA, 2005), however, due to the limited availability of the complex meteorological and surface characteristics data required to run AERMOD, as of April 2007, only a few states required its use (Moore, 2007). Both ISCST3 and AERMOD, run by ISC-AERMOD View software packaged by Lakes Environmental, Inc., were used for modeling lagoon (Idaho) and dairy-wide (California) NH₃ emissions. Both models assume steady-state conditions, continuous emissions, conservation of mass, and a Gaussian distribution in both the vertical and crosswind directions. The two models differ in that ISCST3 assumes a Gaussian distribution of pollutants based on time averaged meteorological data whereas AERMOD uses continuous functions for atmospheric stability determinations and based on the stability will use a Gaussian distribution for stable atmospheric conditions and a non-Gaussian distribution for unstable conditions. DOAS measurements were used in conjunction with the vendor-supporting WindTrax software tool which uses Lagrangian stochastic models for dispersion calculations in both forward and backward modes (Thunderbeach Scientific, 2009).

Emission rates were determined using the ISCST3 and AERMOD models via techniques of inverse modeling. The observed emission rate was determined by comparing modeled concentrations (C_{modeled}) to actual measured values (C_{observed}) at the various receptor locations (see Equation 1). It must be noted that the “observed” concentration was actually the measured downwind concentration minus the average measured upwind concentration to account for local background NH₃ values. The models were prepared using seed emission rates obtained from literature outlined in previous studies. By multiplying these emission rates (E_{seed}) by the ratio of concentrations an observed emission rate could be obtained.
\[ E_{\text{observed}} = E_{\text{seed}} \left( \frac{C_{\text{observed}}}{C_{\text{mod, eled}}} \right) \]  

Equation 1

Results

**Idaho dairy**

Instrumental problems experienced with the SDL FTIR spectrometer and the UV-DOAS located on the east bank of the lagoon lead to little data from the FTIR spectrometer being available and no data was salvageable from the assumed downwind UV-DOAS for analysis.

Measurements gathered from the various measurement techniques were compared. Figure 3 contains a plot of the concentrations measured by the co-located passive sampler and denuder system. Instrument errors were reported as 10% for both the passive samplers (Roadman, 2003) and denuder system (Zhu, 2006). As can be seen, the denuder and the collocated passive sampler showed very good agreement with the notable exception of October 1st, 3rd (AM), 3rd (PM), 5th-6th, and 6 (AM). During the period of October 1st through October 3rd, the passives were operated without an optional rain cap. On the days during this period with excessive differences (1st, 3rd AM and PM), the wind was strongly blowing (6.3-6.7 m/s). It is speculated that without the rain caps in place, the strong advection on these days overtly enhanced the apparent diffusion. This speculation of high wind diffusion enhancement is somewhat supported by a noticeable difference even when the caps are in place when the winds also became strong. This was the case on the last two sampling periods when the wind blew at 5.6 and 10.6 m/s, respectively.

![Figure 3. Comparison of NH₃ concentrations measured by a co-located passive sampler and denuder system adjacent to the Idaho wastewater lagoon. Error bars represent the instrument standard error.](image-url)
A plot of integrated pathlength concentrations measured by the U of I FTIR system and the average concentration measured by passive samplers located along that same pathlength is shown in Figure 4. As with the passive vs. denuder comparisons, the high wind days were not very comparable presumable due to the enhanced diffusion effect on the passive samplers. It should also be noted that the higher passive values shown in Figure 4 due to the averaging of multiple samplers along the lagoon east bank as opposed to the single passive sampler located at the denuder location at the lagoon north-east corner. Furthermore, available west bank UV-DOAS measurements and a passive sampler located on the same bank are plotted in Figure 5.

Figure 4. Comparison of Idaho dairy lagoon east bank pathlength FTIR and average passive sampler measurements. Error bars represent the instrument standard error.

Figure 5. Comparison of UV-DOAS and passive sampler measured NH₃ concentrations from the west bank of the Idaho dairy lagoon. Error bars represent the standard error.
Average NH₃ emission rates determined using the different methodologies are listed in Table 1. It should be noted that the wind tunnel emission rate was determined from measurements taken in one location in the southwest corner of the lagoon and based on the assumption that the lagoon was emitting at the same rate over the entire lagoon surface.

Table 1. Lagoon NH₃ emission rates determined using the various measurement techniques. Uncertainty represents the standard deviation.

<table>
<thead>
<tr>
<th>Methodology</th>
<th>Emission rate µg/m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wind Tunnel</td>
<td>50.4 ± 19.6</td>
</tr>
<tr>
<td>DOAS</td>
<td>20.2 ± 12.7</td>
</tr>
<tr>
<td>Passive Samplers</td>
<td>120.1 ± 85.3 (ISCST3), 135.5 ± 83.2 (AERMOD)</td>
</tr>
<tr>
<td>Denuder</td>
<td>156.7 ± 76.6 (ISCST3), 165.8 ± 65.4 (AERMOD)</td>
</tr>
<tr>
<td>FTIR</td>
<td>69.1 ± 26.1 (ISCST3), 96.6 ± 33.0 (AERMOD)</td>
</tr>
</tbody>
</table>

California dairy

Comparison of downwind FTIR measurements from opposite facing sample pathlengths and the average concentrations measured by passive samplers located along those pathlengths are shown in Figures 6 and 7. As can be seen, generally comparable results were obtained, and both systems were able to characterize the strong difference between the west and east pathlengths. Referring back to Figure 2, it can be seen that the east path was directly downwind of the main lagoon and solid separating pond. Figure 7 does seem to indicate higher values reported by the passive systems; however, this may be due to bias introduced between the integrated samples of the FTIR pathlength and the discrete sample points of the passive samplers.

![Figure 6. Comparison of NH₃ concentrations measured by the FTIR system and passives samplers along the West Tower pathlength. Error bars represent the instrument standard error.](image)
Average NH$_3$ emission rates were determined using the combination of concentrations measured using both the passive samplers and the downwind FTIR system and the ISCST3 and AERMOD models. Emission rates are per area for the lagoon and solid separator and per animal unit for the corrals (see Table 2). The per animal unit (AU) (500 kg live weight) emission rates are based on average animal weights of 1650 lb/head for milk producers and dry cows, 1250 lb/head for a 2 year old heifer, and 90 lb/head for a 1 day old calf, as given by the dairy operator at the California dairy.

**Table 2. California dairy NH$_3$ emission rates derived from passive sampler measurements.**

<table>
<thead>
<tr>
<th></th>
<th>Passive Samplers</th>
<th>FTIR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IS CST3</td>
<td>AERMOD</td>
</tr>
<tr>
<td>Lagoon</td>
<td>µg/m$^2$/s</td>
<td>µg/m$^2$/s</td>
</tr>
<tr>
<td></td>
<td>60.5 ± 40.0</td>
<td>92.7 ± 91.1</td>
</tr>
<tr>
<td>Solid Separator</td>
<td>147.1 ± 27.7</td>
<td>26.5 ± 12.3</td>
</tr>
<tr>
<td>Adult Cattle</td>
<td>81.0 ± 38.3</td>
<td>62.8 ± 42.7</td>
</tr>
<tr>
<td>Calves</td>
<td>100.7 ± 58.1</td>
<td>84.5</td>
</tr>
<tr>
<td>Dairy Facility</td>
<td>102.3</td>
<td>84.5</td>
</tr>
</tbody>
</table>

**Discussion**

Measured NH$_3$ concentrations around the Idaho wastewater lagoon were found to be similar for the different measurement techniques. The comparisons of the denuder and passive samplers and the passive samplers and FTIR spectrometer found very similar values for all but three sampling periods (October 1, October 3 AM and PM). This discrepancy was attributed to the fact that during the first five sampling periods the protective caps were left off of the passive
samplers, and, during the three specified periods fairly strong winds were observed. It was assumed that without the protection of the caps excess NH₃ was forced onto the sample collection pads and therefore these measurements cannot be considered reliable. A similar result can be seen in the comparison of the passive sampler and UV-DOAS. Similar concentrations were found except during the October 2 AM sampling period when this sampler was at the downwind side and the passive sampler protective cap was absent. It should be noted that other sources of disagreement between the passive sampler and UV-DOAS system include that the only measurements made by the DOAS located on the west bank used for calculations were those when the wind was blowing between 45 and 135 degrees (NE to SE), which left little data available for analysis and that the DOAS yields path integrated concentrations as opposed to the sampler only representing the concentration at a single point.

With the exception of the DOAS and a discrepancy between the wind tunnel and denuder system, the five different methods utilized during the Idaho campaign yielded emission rates that were statistically equivalent. Again, it should be noted that the DOAS emission rates were determined using somewhat incomplete data. Sources of error in these flux calculations include the differences between point (passives, denuder, wind tunnel) and path integrated (FTIR, DOAS) receptor instrumentation. Also, it was assumed in making these calculations that the entire lagoon was emitting NH₃ at the same rate. While this is likely a good approximation, variations in flux may exist due to differences in lagoon depth and temperature over the entire area of the lagoon.

A comparison of concentrations measured by passive samplers and the downwind FTIR system at the California dairy found that the average passive sampler concentrations more closely reflected those path integrated concentrations measured for the pathlength towards the West Tower reflector location as opposed to the East Tower location. This was likely due to the different sources and proximity of the sources to the sample path. The east pathlength passed very closely to the solid separator and some of the cattle pens, whereas the west pathlength was influenced by fewer sources at a greater distance.

Data from the California dairy, where only FTIR and passive samplers were compared, yielded emission rates that were also statistically equivalent. Emission rates from the lagoon and solid separator were reported on a per unit area basis whereas corral emission rates were reported on a per animal unit basis. It should be noted that the housing conditions at this facility were open and scraped corrals.

Emission rates derived for the Idaho wastewater lagoon using the two models used in this study, ISCST3 and AERMOD, were found to have no statistical difference. This, however, was not necessarily the case for the models run for the California data. The variations in the California rates are due in a large part to the combined nature of the NH₃ plume from the dairy. This created difficulty in assigning a seed emission rate to accompany each receptor observed-to-modeled concentration ratio. It should also be noted that the ISCST3 model often predicted nearly opposite plume spreading from that observed in the AERMOD models. An example of this is shown in Figures 8 and 9.
The direction of the plume propagation predicted in the ISCST3 model consistently indicted that most of the receptors where the largest concentrations were being measured, were to be considered background concentrations. For this reason, background NH$_3$ was neglected in the calculation of flux when utilizing the ISCST3 model. It is postulated that the ISCST3 model was inadequate in handling the meteorology variations of the 12 hour sampling periods.

A comparison between the emission rates derived for the different dairies is also in order. The flux calculated using measurements from the passive samplers and the two modeling programs from the Idaho dairy lagoon and California dairy lagoon was found to be 120.1 ± 85.3 µg/m$^2$/s (ISCST3) and 135.5 ± 83.2 µg/m$^2$/s (AERMOD) and 60.5 ± 40.0 µg/m$^2$/s (ISCST3) and 92.7 ± 91.1 µg/m$^2$/s (AERMOD), respectively. FTIR measurements in combination with the AERMOD model yielded values of 96.6 ± 33.0 µg/m$^2$/s for Idaho and 86.6 ± 51.1 µg/m$^2$/s for the California dairy. In both cases, it was found that similar emission rates existed for NH$_3$ from the
wastewater lagoons from each dairy, despite rather differing meteorology conditions and lagoon size. Table 3 contains a summary of some emission rates from wastewater lagoons and dairy cattle housing from studies conducted by other researchers as well as this study. The emission rates determined in this study are similar to these literature values.

Table 3. NH3 emission rate comparisons.

<table>
<thead>
<tr>
<th></th>
<th>Emission rate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lagoon - This Study</strong></td>
<td>µg/m²/s</td>
</tr>
<tr>
<td>Idaho dairy</td>
<td>20.2 - 165.8</td>
</tr>
<tr>
<td>California dairy</td>
<td>60.5 - 92.7</td>
</tr>
<tr>
<td><strong>Comparison Lagoon Studies</strong></td>
<td>µg/m²/s</td>
</tr>
<tr>
<td>Arogo et al. (2006)</td>
<td>459.4</td>
</tr>
<tr>
<td>Sheffield &amp; Louks (2006)</td>
<td>101.9</td>
</tr>
<tr>
<td>Todd et al. (2001)</td>
<td>38.2 – 97.2</td>
</tr>
<tr>
<td><strong>Housing – This Study</strong></td>
<td>g/d/AU</td>
</tr>
<tr>
<td>California dairy</td>
<td>62.8 – 82.9</td>
</tr>
<tr>
<td><strong>Comparison Dairy Cattle Studies</strong></td>
<td>g/d/AU</td>
</tr>
<tr>
<td>Cassel et al. (2005)</td>
<td>50.5 - 104</td>
</tr>
<tr>
<td>Ferm et al. (2005)</td>
<td>5.1 - 31.7</td>
</tr>
</tbody>
</table>

**Conclusion**

Ammonia concentration measurements were made on two separate dairy facilities utilizing a variety of measurement techniques including passive diffusion samplers, an annular denuder, DOAS, FTIR, and a wind tunnel system. These measurements were then used in combination with two EPA models, ISCST3 and AERMOD, to determine emission rates from wastewater lagoons and from the dairy as a whole. Concentration data from the different measurement techniques were similar, especially when homogeneity of sources along sample pathlengths existed. Emission rates were determined for sources at both sampling locations. From the Idaho campaign, a dairy wastewater lagoon emission rate found using the assorted measurement and modeling techniques varied from 20.2 ± 12.7 to 165.8 ± 65.4 µg/m²/s. An overall dairy emission rate of 84.5-107.3 g/d/AU, including emissions from the cattle housing, wastewater lagoon, and solid separator, was determined from the California campaign.

**References**


U.S. EPA. 2005. Revision to the Guideline on Air Quality Models: Adoption of a Preferred General Purpose (Flat and Complex Terrain) Dispersion Model and Other Revisions;