

Developing Appropriate New Technologies



Novel FTIR and Laser Spectroscopy Methods for Measuring Trace Gas Emissions from Agriculture and Forests

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Abstract

This paper describes novel infrared spectroscopic methods to measure emissions of trace gases to the atmosphere from agriculture and forests. These methods address the need for non-intrusive, on-farm and field measurements of emissions from animals, plants and soils without disturbing them so that the measurements are truly representative. Fourier Transform Infrared (FTIR) spectroscopy enables simultaneous real-time field measurements of CO₂ (+ ¹³CO₂), CH₄, N₂O, NH₃ and H₂O (+ HDO) with a single instrument in both sampled air and over open paths downwind of agricultural sources. Infrared lasers, in particular near infrared lasers derived from recent developments in telecommunications, are available for a range of species and their isotopomers and capable of fast repetitive measurements, but only on a one laser - one species basis. The paper describes two examples of applications using open and closed path FTIR and laser spectroscopy: a tracer method for measuring methane emissions from free-ranging cattle, and tower measurements of CO₂, N₂O, CH₄ and H₂O exchange including isotopic fractionations in CO₂ and H₂O in a 40m eucalypt forest.

Fourier Transform Infrared and Laser Spectroscopy

Over the past decade, at the University of Wollongong we have developed Fourier Transform Infrared (FTIR) spectroscopy as a method for simultaneous real-time analysis of several trace gases in air with high precision and accuracy in a field instrument. FTIR spectroscopy is a broad-band technique which measures the absorption of infrared radiation over a wide spectral region, typically 500-4000 cm⁻¹ (2.5 – 20 μm). Several trace gases of interest to agricultural air quality absorb in this region, including CO₂, CH₄, N₂O, CO and water vapour. Isotopic species ¹³CO₂ and HDO can also be determined, providing a method for real-time field measurements of δ¹³C in CO₂ and δD in H₂O. For air sampled into a cell ("closed path"), precision and accuracy of 0.1% can be obtained for concentrations, and better than 1‰ for isotopic fractionations. Measurement times range from a few seconds to a few minutes. FTIR is also suited to open path measurements over paths up to a few hundred metres, with slightly reduced accuracy relative to closed path measurements.

By comparison, in laser spectroscopy a single infrared frequency is scanned across a narrow spectral range containing one or two absorption lines of a single gas. Laser instruments are thus typically tuned to a single gas or isotope ratio, but the laser source provides high signal:noise ratios and can provide high precision at >1Hz measurement frequency. Laser spectroscopy is therefore well suited to eddy covariance and other techniques requiring fast measurements. Mid infrared lasers are available for a wide range of species, but normally require liquid nitrogen-cooled lasers and detectors. More recently, relatively inexpensive near infrared lasers emerging from telecommunications developments have been applied to spectroscopy. These are compact, low power devices that do not require liquid nitrogen cooling, and are well suited to field applications. New laser technologies are continually developing.

In this paper we describe two examples of novel applications to agricultural and forest measurements which exploit the multi-species, high precision advantages of FTIR spectroscopy.

Methane Emissions from Free Ranging Cattle

To each animal in a small (ca. 20) herd, we attach a canister on a halter which releases a tracer gas at a measured rate – we use nitrous oxide (N₂O) as the tracer because it is safe and can be determined

accurately at low levels by FTIR at a release rate of ca. 10 g hr^{-1} or 240 g day^{-1} per head. The cattle are free to graze normally in ca. $50 \times 50\text{ m}$ area. We have shown through trial gas releases (Figure 1) that when the tracer and methane emissions are co-located, the plumes remain well mixed downwind. We setup an open-path FTIR system over a path of 50-200m downwind of the cattle enclosure, and monitor the CH_4 and N_2O concentrations continually with typically 2 minute time resolution. For each measurement period, the ratio of the fluxes or emission rates (F) from the cattle equals the ratio of the excess concentrations above background downwind (C), and the emission rate of methane can be calculated from

$$F(\text{CH}_4) = F(\text{N}_2\text{O}) \cdot \frac{C_{\text{CH}_4}}{C_{\text{N}_2\text{O}}}$$

The measurements thus provide a continuous herd-average emission rate. Results from trials in 2005 will be presented.

Figure 1 demonstrates the excellent correlation between two gases (in this case N_2O and NH_3) released at equal rates from adjacent gas cylinders and measured in an open path 100 m downwind, confirming the validity of the tracer method. Figure 2 shows the tracer canister mounted on a cow, and the open path FTIR spectrometer.

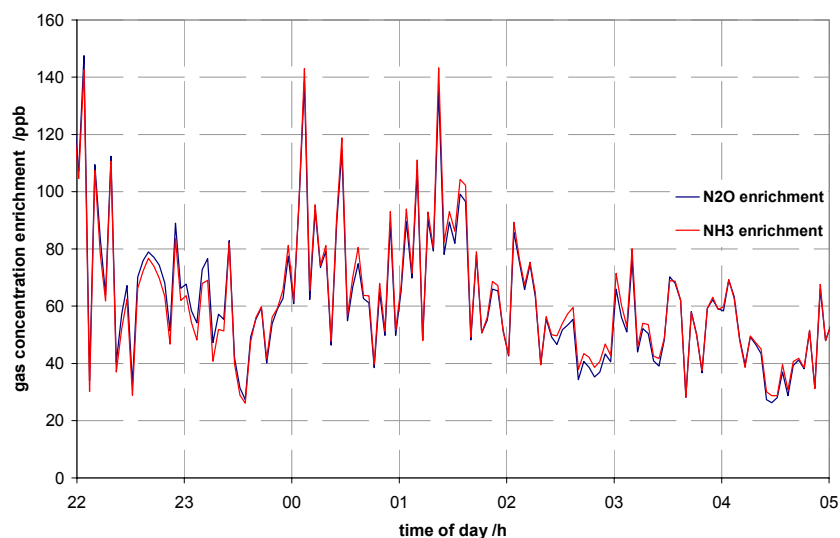


Figure 1. Concentrations of N_2O and NH_3 measured over an open path 100m downwind of controlled releases of 5 std L min^{-1} of each gas. These measurements demonstrate that to a very good extent the gases remain well mixed when released from the same location.



Figure 2. The open path FTIR spectrometer (left) and tracer release canister mounted on a grazing cow (right)

Surface-Atmosphere Exchange of Trace Gases Field Measurements of δD in Water Vapour and $\delta^{13}\text{C}$ in CO_2

Isotopic fractionations in water vapour and carbon dioxide provide powerful data to understand soil- plant-atmosphere exchange of water and carbon and constrain models. We have optimised closed path FTIR analysers for measurements of the $\text{HDO}/\text{H}_2\text{O}$ ratio in water vapour and $\delta^{13}\text{C}$ in CO_2 , thus providing a method for continuous field measurements of these fractionations. In 2005 took part in a 2-week campaign at the Tumbarumba Ozflux forest site in SE Australia. From a 70 m tower in mature eucalypt forest with a 40 m canopy we obtained 2 weeks of continuous 7-point vertical profiles of water vapour and its D/H ratio as well as profiles of CO_2 , CH_4 , N_2O and CO with excellent precision and reliability. In all we obtained over 5000 measurements of each species in real time. Preliminary results from the analysis will be presented. Figure 3 presents on overview of the δD in water vapour data.

Conclusions

FTIR spectroscopy provides a new tool for accurate and precise multi-species analysis of trace gases in air, with many potential applications to agricultural air quality.

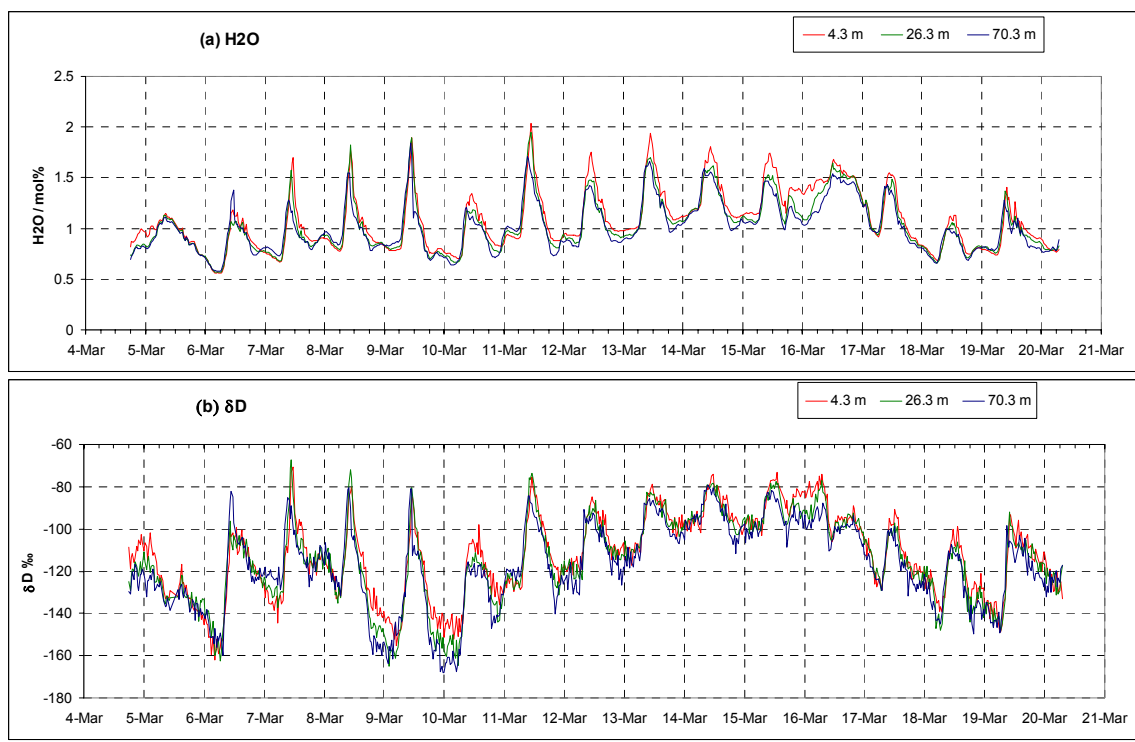


Figure 3. Continuous vertical profiles of water vapour concentration (upper) and deuterium fractionation δD in H_2O (lower) over two weeks in a 40 m eucalypt forest

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The following reviews provide further reading on FTIR and laser spectroscopy applications to atmospheric trace gas analysis.

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*This special issue of *Isotopes in Environmental and Health Studies* contains many papers from the Stable Isotope Ratio Infrared Spectrometry conference, Vienna 2004.



Direct, Fast Response Measurements of Gas-Phase Ammonia

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Abstract

Gas-phase ammonia is implicated as an important particle formation catalyst. As a ubiquitous bi-product of amino acid decomposition, it is tough for animal husbandry and other agricultural facilities to control. However, the U.S. Environmental Protection Agency is mandated to regulate the emission and formation of fine particulate matter (PM 2.5). It is likely that farmers will soon also be regulated for ammonia emissions, yet these remain difficult to measure. At NASA Langley, a photothermal interferometer has been designed and built to make fast gas-phase ammonia measurements for ammonia flux and emissions estimates at agricultural facilities. Ammonia is difficult to measure due to its basic and polar nature, and existing measurement techniques generally suffer from long measurement integration times, measurement interferences, or complexity and expense of instrumentation. We have designed and built an instrument that can be run autonomously, with a continuous zero, to make measurements of ammonia at 1-second time resolution and sub-ppb sensitivity. We present the results of our calibration and field-testing of the instrument, along with preliminary measurements of the diurnal variation in ammonia emissions from an animal feeding facility.



Use of Elastic Lidar to Examine the Dynamics of Plume Dispersion from an Agricultural Facility

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Abstract

The issue of odors and noxious chemicals from large scale animal husbandry activities is an increasingly large problem in a number of states, particularly Iowa. The goal of this project is to understand the manner and pathways in which emissions from animal husbandry facilities occurs and how it is transported downwind. Evidence is presented that demonstrates that current assumptions about the manner in which pollutants are emitted from these facilities are not correct. Contrary to current assumptions, the emissions are not along the surface, are not continuous, and bear little resemblance to commonly used Gaussian plume models. Remediation activities and emissions estimates based on these assumptions, may well be ineffective. If we are ever to devise effective remediation strategies, they must be based on a comprehensive understanding of the actual phenomena.

Introduction

The current trend in livestock husbandry in the United States is toward increasing industrialization which brings with it, the utilization of new technologies, the concentration of production and processing facilities, and the integration of the individual parts of the process from production, through processing, and marketing. This trend can be identified by increases in the overall size of the facilities, the average number of animals per farm, and the use of advanced animal confinement systems. The increasing size of these facilities is due to the perception that large operations benefit from an economy of scale, particularly in terms of expenditures for labor, feed, and permanent facilities (SOTF, 1995). The industrialization, consolidation, and concentration of animal production in the U.S. is not unique to any single livestock group. It has been a trend in all of the major livestock types including cattle, dairy, swine and poultry industries.

A result of the concentration of livestock and poultry industries has been large, concentrated quantities of animal wastes with the associated concerns of odor, air and water quality pollution. There is a great deal of research that supports the concern that airborne dust, bioaerosols, gases, and endotoxins from animal confinement facilities can affect both human and animal mental and physical health (Schiffman et al., 1995; Cunnick, 1995; Donham, 1998a; Donham, 1998b; Homes, 1995). In addition, the presence of nearby livestock facilities may lead to decreased real estate values (Hudson, 1998; Colindres, 1998; Palmquist, 1997) and negative effects on recreation and tourism (Okun, 1997).

There are a number of different ways to model odor emissions and air quality. However, Gaussian models are used most often because of their relative mathematical simplicity (Li et al., 1995). The Gaussian plume dispersion equation is a mathematical model that predicts the downwind concentration of a non-reactive effluent in space and time as a function of the initial concentration, the downwind distance traveled, the crosswind distance and height of the measurement, the height of the emission source and the turbulent properties of the wind (Gassman, 1995; Gassman, 1992). It assumes that the atmosphere is diffusive. Modifications to the Gaussian plume model that better represent agricultural sources have been investigated (for example, Gassman, 1995; Keddie, 1980). Turbulent flows, such as the flow over irregular or rugged terrain and those in the lee of obstacles, are considered exceptional and non-Gaussian and for which there have been attempts to develop modified Gaussian models (for example, Krause, 1994; Cha and Jann, 1990). A detailed discussion of transport from ground level agricultural sources can be found in Smith (1993).

While there has been a great deal of research on the issues associated with the changes in livestock husbandry, most of the measurements that have been made have assumed that the source of the emissions is at or very near the ground and that the sources are continuous, similar to the emissions from a smokestack. They have further assumed that conventional Gaussian diffusion models are appropriate to describe the downwind dispersion of the plume from the facilities (for example, Piringer and Schauburger, 1999). For ventilated facilities, the primary source of effluents is often assumed to be the exit aperture of the ventilation fans (Demmers et al., 1998, 1999). Similarly, measurements made with Fourier Transform Infrared Spectrometers (FTIR) are often made over several paths. A bivariate Gaussian shape is assumed and fitted to the available data so as to reconstruct the details of the distribution in the plume and the shape (for example, Hashmonay et al., 1999a, 1999b; Price, 1999, Childers et al, 2001; Harris et al., 2001). All of these measurements are dependent upon assumptions of the shape and size of the emitted plume. As we shall show, this plume is not well-modeled by a Gaussian shape.

Site Overview

This study was conducted at a commercial swine production facility located in Boone County in north-central Iowa. The operation consists of 3 confinement barns, with an anaerobic pit underneath each individual barn, which collects swine urine and manure. The three confinement barns are bordered by a cornfield to the north and west, a soybean field to the east, and to the south, is bordered by 180th Street and a soybean field on the other side. Figure 1 is a diagram of the facility.

Each hog confinement barn houses approximately 1200 head of hogs. The three confinement barns are oriented lengthwise in an east-west direction to make use of the prevailing southerly breezes during the summer months for ventilation. The entire complex covers a distance of 80 m in both north-south and east-west direction. Each confinement barn is approximately 12 m wide and 80 m long. The barns are spaced approximately 21-22 m apart. Each anaerobic pit underneath the confinement barns has an approximate depth of 20 ft. On each hog barn there are six fans, three on the north and 3 on the south sides of the barns. Two of the three fans are pit fans with an approximate diameter of 24" that run continuously. Along with the two pit fans is one large 4' diameter fan that is located in between the two pit fans, and turns on when the temperature inside the barn exceeds a certain temperature value. Curtains are placed on both the north

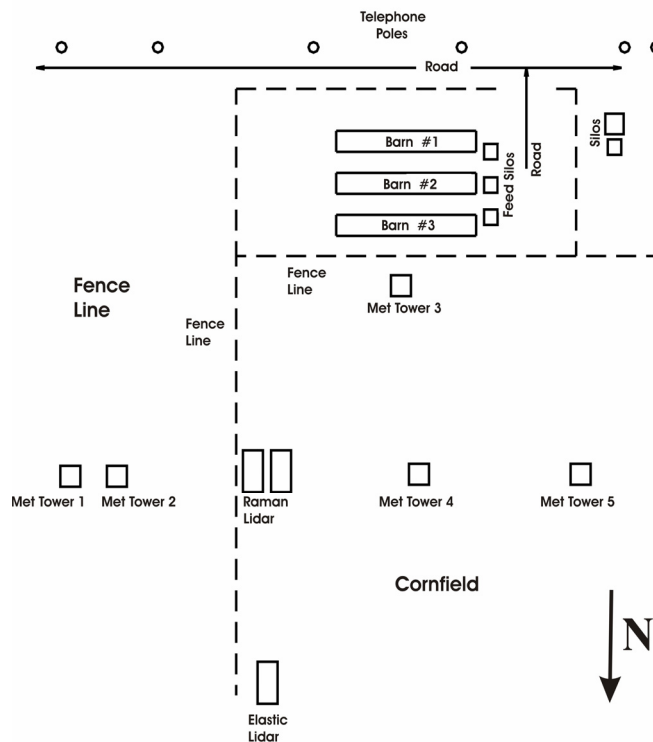


Figure 1. The schematic layout of the experiment

and south sides of the hog barns and are operated by a temperature sensor, lowering when the temperature inside the hog barns exceed a certain temperature.

Approach

Laser radars (lidars) are instruments that can map the three dimensional concentrations of certain components of the atmosphere. This allows the measurement and visualization of larger scale atmospheric flows. If the measurements can be taken fast enough, the evolution of the flow can be measured. Elastic lidars measure the backscattering from particulates. Raman lidars measure the absolute water vapor concentration. The IIHR scanning miniature lidar (SMILI), is a small, scanning lidar that was designed to use elastic backscattering to determine the distribution and properties of atmospheric particulates (figure 2). The lidar operates by emitting a pulse of infrared laser light into the atmosphere. Particulates interact with the pulse and scatter light back to the lidar. The term elastic refers to scattering in which no energy is lost by the photons, so that the detected light is at the same wavelength as the emitted light. The amount of returning light collected by the telescope is proportional to the cross sectional area of the water droplets in the air and the amount of atmospheric attenuation. The system is capable of both day and night operation.

A Nd:YAG laser operating at 1.064 (or 0.532) microns is the laser source. The laser is attached to 0.25 m, f/10, Cassegrain telescope. The laser beam is emitted parallel to the telescope after going through a periscope. The telescope-laser system is able to turn rapidly through 200 degrees horizontally and 100 degrees vertically using motors incorporated into the telescope mount. The system is entirely computer controlled through the use of various cards in the PC. This enables high speed data transfer and control of



Figure 2. A photograph of the miniature elastic lidar set up to map particulates in the field. This instrument took the data in figures 3 and 4.

the scanning motors, which allows the system to scan rapidly. The lidar can be operated remotely and autonomously, using preprogrammed sequences which require an operator only to start.

Because the backscatter cross section for elastic scattering is large in comparison to most optical scattering processes, a small laser and telescope can be used and much faster time resolution is possible. The scanning system can be used to create vertical scans (also known as Range-Height Indicator or RHI scans) showing the relative particulate scattering within a vertical slice of the boundary layer. These can be done with a time resolution of less than 6 seconds. The small size of the lidar coupled with its fast scanning capability and sophisticated scanning and analysis methods make this lidar unusually capable and versatile.

The ability to measure particulates quickly is fortuitous in that particulates are a component of odor plumes and are closely related to odor from cattle, swine and poultry facilities. Many odorous compounds are easily absorbed onto and carried by particulates (Laird, 1997, SOTF, 1995). In a given volume of air, particulates may have absorbed many times the amount of some odorous compounds than is found in vapor form in the same volume of air. Particulates then concentrate some of the more obnoxious odors (OCTF, 1998). The importance of dust in the transportation of odor from livestock buildings has been well documented (OCTF, 1998; Thernilius, 1997; Laird, 1997; SOTF, 1995; Carpenter and Mouldsley, 1986; Hartung, 1986; Hammond et al., 1979; 1981; Hammond and Smith, 1981).

Water vapor is another indicator of the pathways that chemical species associated with animal waste might take. Since water vapor is a major component of animal waste and is similarly volatile, the concentration of water vapor should be an indicator of the concentrations of trace chemical species emanating from the waste. Water vapor is present with much higher concentration than other chemical species and is easily measured with a Raman lidar.

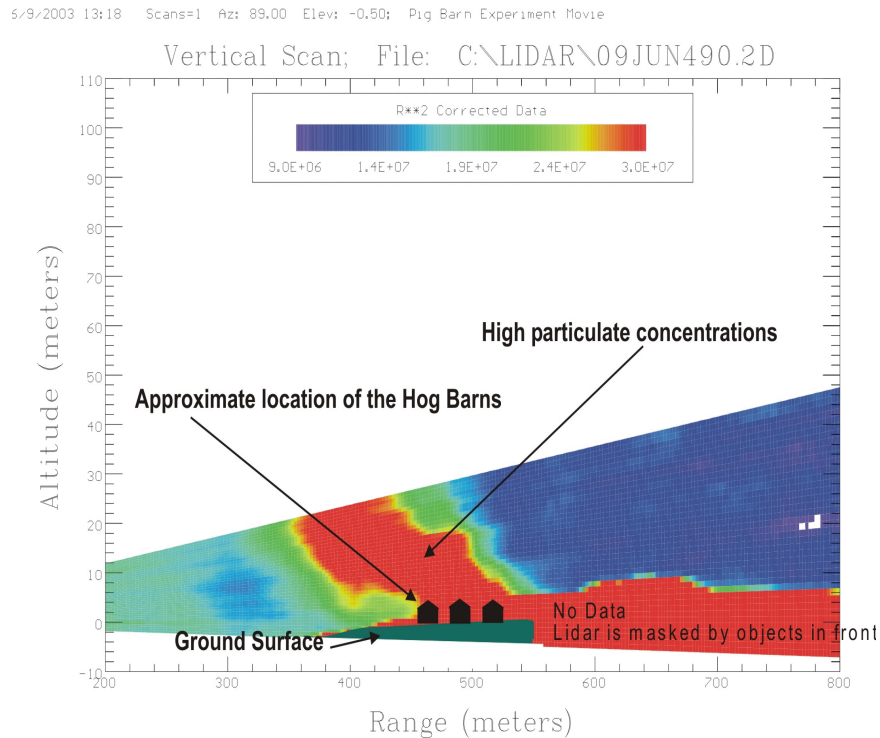


Figure 3. A lidar scan showing the relative particulate concentrations in a vertical slice through the atmosphere. The location of the ground surface and the three barns has been added to show their location. Blue colors indicate regions of low particulate concentration and reds indicate areas of high concentration. The size and height of the plume from the facility was completely unexpected.

The Raman water vapor lidar is an instrument that uses Raman backscattering to determine the concentration of water vapor along a line of sight in the atmosphere. The device operates by emitting a pulsed ultraviolet laser beam into the atmosphere. Nitrogen gas and water-vapor react to this light via the Raman scattering process, causing light of longer wavelengths to be scattered back to the lidar. During the day, the system operates in the solar blind region of the spectrum using krypton fluoride as the lasing media to obtain light at 248 nm. The Raman-shifted nitrogen signal returns at 263 nm and the Raman-shifted water-vapor signal returns at 273 nm. At night, when the solar background light is negligible, other wavelengths may be used. Since wavelengths longer than 300 nm are not strongly absorbed by atmospheric ozone, and Rayleigh scattering is reduced at longer wavelengths, greater range is possible at night than in the day. Simultaneous measurement of the water-vapor and nitrogen returns provides a simple method for obtaining absolute measurements of water vapor concentration. A more complete explanation of the working of this instrument can be found in Eichinger et al., (1999).

In late June of 2003, and August of 2005, a team from the University of Iowa, Los Alamos National Laboratory, and the National Soil Tilth Laboratory conducted a campaign to examine these assumptions. A particulate and a Raman water vapor lidar were used to examine the air flow around the three hog barns described above. The lidars were oriented so that their primary line of sight was perpendicular to the long axis of the facilities and roughly parallel to the mean wind direction. Water vapor emissions should be related to emissions from sewage and particulates are strongly related to odors. Both should be emitted and transport downwind just as the more dilute noxious chemical species are emitted and transported. Both water vapor and particulates should be good surrogates with which to address the problem.

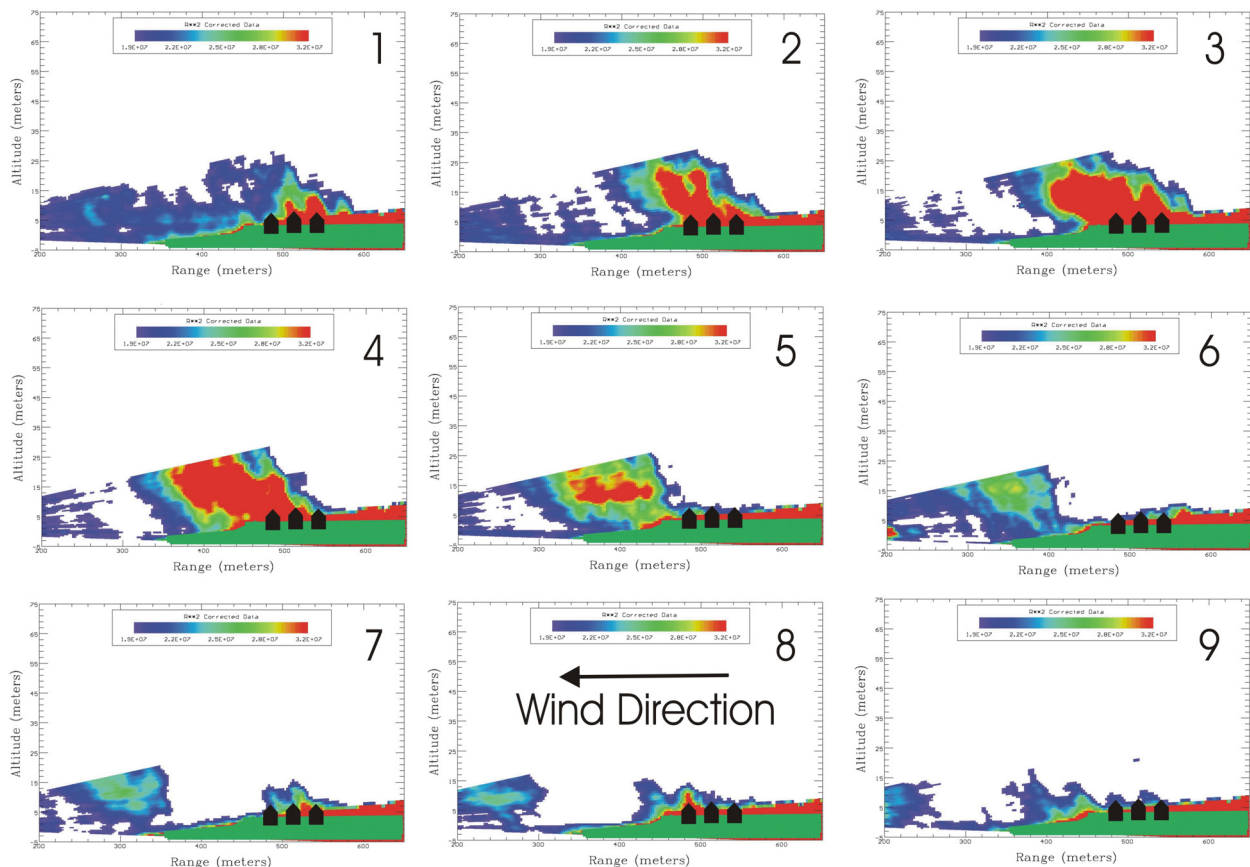


Figure 4. A sequence of lidar scans spaced approximately 8 seconds apart. The development of the plume can be seen by the third figure. The plume then translates down wind.

Before collecting data with the miniature elastic lidar and the Raman lidar, distances from the two-lidar systems relative to the hog barns were measured with the miniature elastic lidar. The physical path length from the miniature elastic lidar to the hog confinement barns was approximately 500m. Measurements were taken with the miniature elastic lidar and the Raman lidar at this site on the 3rd, 9th, 10th, and 11th of June 2003. For measurement purposes of wind direction, wind speed, and temperature, five 3D sonic towers were set up in the corn field north of the complex and in the soybean field to the north-east. On the 3rd, 10th, and the 11th, the wind direction was primarily from the north-north east, whereas on the 9th wind direction was primarily from the south. Throughout the two-week duration of the experiment, the 3D sonic anemometers were constantly taking wind speed and wind direction measurements. Chemical detectors were also mounted on each of the five towers with the 3D sonic anemometers to measure the chemical composition of the plumes coming off from the hog complex. Figure 1 shows the placement of the five towers.

Lidars are not a new technology, but the ability to rapidly scan the lidar so as to generate successive images of the concentration of an atmospheric constituent is rare. Mapping the atmospheric quantities in three dimensions with time allows one to trace the nature of the flow. It also allows visualization of the flow, leading to clearer understanding. It will not replace point sensors that measure concentrations of trace atmospheric compounds. However, it provides the context in which those measurements should be interpreted.

Data Collected

Vertical scans were taken of the hog confinement barns on the 3rd and 9th, and horizontal scans were taken of the complex on the 11th using the miniature elastic lidar. Information from the lidars indicates that the source of emissions from these facilities is not “near the surface”, is not continuous, and is not Gaussian in nature. Figure 3 is an example of a lidar scan showing the relative aerosol concentrations in a vertical slice of the atmosphere roughly centered on the barns and parallel to the mean wind. The location of the barns is indicated on the figure. As can be seen from figure 3, the emissions are lofted high into the sky (30 to 50 m). The ability of the lidar to rapidly scan makes it possible to make repeated scans with a time separation of as little as 6 seconds. Examination of successive scans made nearly parallel to the wind direction reveals that the emissions are in the form of “puffs”. A large, intense plume will be emitted in a near vertical direction and then will be transported with the wind. As it travels downwind, the plume expands and diffuses. Figure 4 is a sequence of lidar scans showing the growth of a “puff” and then its transport downwind. The emission of these “puffs” is regular, so that there is seldom a period longer than about 30 seconds with no activity, but there was not a period that was clearly dominant. The first and last of the panels in figure 4 show the remnants of a previous “puff” and the beginnings of the next “puff.”

The fact that the emissions are not continuous is significant. Most measurements of trace chemical species measure averages over some extended period. However for toxicological purposes, it is necessary to know the maximum likely exposure (concentration). Periodic emissions, like these “puffs” are areas of much higher concentration than the average. This is important in determining the rates of chemical reactions and may be important in determining the risk factors for human or animal exposure. Further, these emissions are lofted much higher than conventional plume models would indicate. Thus emissions based on a Gaussian plume model would seriously underestimate the total emission.

To determine the characteristics of the plume a section of the data is taken from each scan in a series.

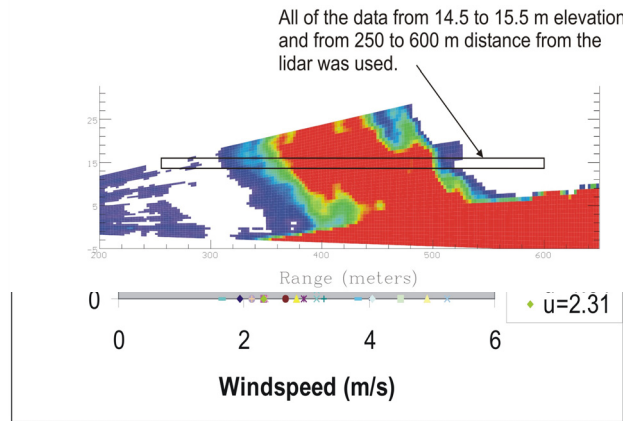
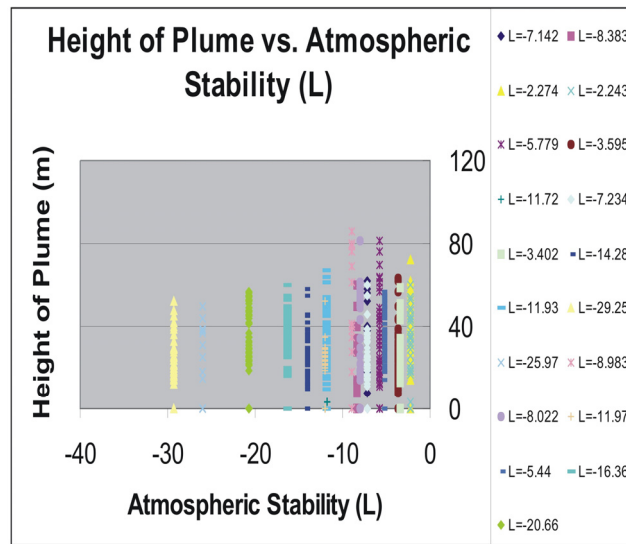


Figure 5. A plot of the maximum height of the plume as a function of the average wind speed. The height of the plume does not appear to be related to the wind speed.
Figure 6. A plot of the maximum height of the plume as a function of the atmospheric stability as measured by the Monin-Obukhov length, L. The height of the plume does not appear to be related to stability.
Figure 7. A plot of a plume with an explanation of how the growth of the plume was studied.

The question of the cause of the lofting remains. There are two classes of possibilities. The first is



mechanical turbulence. This would be caused by the wind traveling over relatively flat terrain and encountering an obstruction (in the form of the barns). The obstruction will disturb the mean flow and cause turbulence. The kinetic energy removed from the mean flow will cause lofting of the air around the barns. The observed plumes could be a form of vortex shedding often found on the lea side of large obstructions.

For mechanical turbulence, the amount of turbulence is roughly proportional to the velocity of the mean flow. As the wind speed increases, one would expect that the increased level of turbulence would loft the plume higher. As can be seen from figure 5, there seems to be no relationship between the maximum height of the plume and the wind speed. The second possibility is buoyant lofting of the plume. With this mechanism, a parcel of air is warmed near the surface and is lofted because of the density differences between the parcel of air and the ambient air. With buoyant lofting, the rate at which the parcel lofts should be a function of the size of this temperature difference. Because of this, one would expect that the height and rate of rise would be related to the stability of the atmosphere. Using the Monin-Obukhov length, L , as the measure of stability, the heights were compelled to L . Again, no relationship is clear. Further, plumes generally rise at speeds of less than 1 m/s. These plumes rose at speeds of up to 5 m/s, more indicative of mechanically generated turbulence.

The rate of growth of the plume was studied by taking cross sections through the puffs at a constant height. After the plume has detached from the barns, all of the data from a narrow altitude band is used to fit a Gaussian function modified to account for the fact that the air upwind is cleaner than the air downwind of the facility. Fitting to this function allows determination of the location of the centroid and the width of the puff at each time. Measuring these at successive times allows one to estimate the velocity and acceleration of the puff as well as the rate of growth. Figures 7, 8, and 9 are examples of data obtained in this manner. As can be seen, the motion of a plume can be tracked in detail and the rate of growth of the puff can be determined. With this information, the average downwind concentrations can be estimated as the sum of all of the puffs that translate by.

The data is then fit to an equation of the form:

$$Concentration = C_1 \exp \left[\frac{(x - x_{centroid})^2}{2\sigma^2} \right] + C_2 x + C_3$$

This is a Gaussian plume superimposed on a spatially varying background. The background aerosol concentration is higher downwind of the barns.

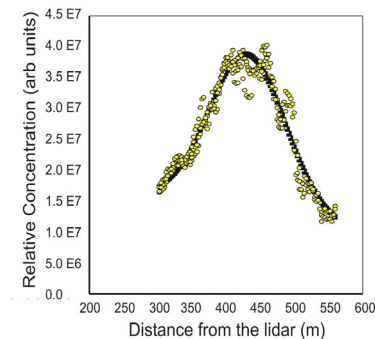


Figure 8. A plot the data from a puff plotted against its fitted function of the form shown above the figure

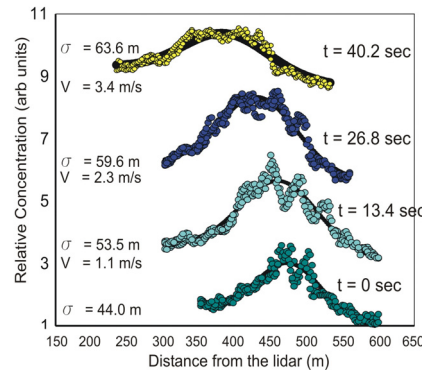
The rate of growth of the plume was studied by taking cross sections through the puffs at a constant height. After the plume has detached from the barns, all of the data from a narrow altitude band is used to fit a Gaussian function modified to account for the fact that the air upwind is cleaner than the air downwind of the facility. Fitting to this function allows determination of the location of the centroid and the width of the puff at each time. Measuring these at successive times allows one to estimate the velocity and acceleration of the puff as well as the rate of growth. Figures 7, 8, and 9 are examples of data obtained in this manner. As can be seen, the motion of a plume can be tracked in detail and the rate of growth of the puff can be determined. With this information, the average downwind concentrations can be estimated as the sum of all of the puffs that translate by.

Conclusion

While the campaign here lasted only for a few days and represents just one configuration of buildings, the facility is typical of its type in Iowa. Further, the type of emissions that were observed occurred during every observation period regardless of the direction or speed of the wind, the stability of the atmosphere, or the operational state of the ventilation fans in the facility. There is some anecdotal evidence that the curtains that govern ventilation in the side walls of the barns may play a role in the regulating the intensity of the plume.

Conventional measurement techniques that have been applied to the problem of emissions from animal operations provide information about the types and concentrations of the emissions at the point the measurement is made, but nothing about the larger scale flow of air that occurs around it. That information must be assumed. As can be seen in the lidar data, the manner in which effluents are emitted is not consistent with conventional Gaussian plume techniques with near surface source regions. The application of lidar in this way for the analysis of emission and flow will provide the context in which conventional measurements should be evaluated. This is necessary if mitigation efforts are to succeed.

Comparison of the fitting constants allows the determination of the centroids, diffusion coefficients, and plume velocity.



Note that the plume expands as it moves downwind and accelerates as it goes.

Plots are offset vertically for clarity.

Figure 9. A plot of several fits to the modified Gaussian function. As can be seen, the downwind location increased in time (indicating acceleration as well as horizontal motion). The puffs also expand in time, becoming more diffuse.

Conventional measurement techniques that have been applied to the problem of emissions from animal operations provide information about the types and concentrations of the emissions at the point the measurement is made, but nothing about the larger scale flow of air that occurs around it. That information must be assumed. As can be seen in the lidar data, the manner in which effluents are emitted is not consistent with conventional Gaussian plume techniques with near surface source regions. The application of lidar in this way for the analysis of emission and flow will provide the context in which conventional measurements should be evaluated. This is necessary if mitigation efforts are to succeed.

Several questions remain. The degree to which aerosols and water vapor can be used as a surrogate for emissions of trace molecular species, for example ammonia, will be tested in field experiments in May of 2006 using multiple sensors for each species. If these species are emitted in the same way and travel together, then they should obey similarity theory. In addition, detailed measurements will be made to address the origin of the plumes. Again multiple instruments will detail concentration and turbulence parameters at the same time and locations as the lidar “sees” a plume emerge. Precise timing and position measurement will be required.

In order that the emissions from animal husbandry activities be quantified, or actions taken to mitigate the effects of these activities, the manner in which emissions occur must be known and understood. The data from the lidars indicates that our current models for emissions from structures housing animal activities poorly predict the large scale features. The limited amount of data available suggests that puffs such as this are emitted intermittently, yet consistently, by the facility and seem to dwarf the emissions from exhaust fans in the facility. None of the current theories for emissions or transport predict or account for this. With the use of state of the art lidars, the particulate and water vapor content of the air above and around these facilities can be mapped. Using this information as well as supporting meteorological information, how and why these emissions occur can be determined.

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Measurement of Volatile Sulfur Compounds Associated with Animal Feeding Operations

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Abstract

Volatile sulfur compounds (VSCs) are a major class of chemicals associated with odor from animal feeding operations. Identifying and quantifying VSCs in air is challenging due to their volatility, reactivity, and low concentrations. In this study, a canister based method is presented that allows for the analysis of VSCs in ambient air at the sub-part-billion range. This technique uses whole air sampling with fused silica lined (FSL) mini-canisters (1.4 L). Canisters are sampled using a heated robotic autosampler and are cryofocused onto the GC column and analyzed in parallel with a MS (mass spectrometer) and PFPD (pulsed flame photometric detector). The GC column effluent was split 20:1 between the MS and PFPD. The PFPD equimolar sulfur response enhances quantitation and the location of sulfur peaks for mass spectral identity. However, transfer of VSCs in the canister GC system was not uniform as evidenced by magnitude of calibration slopes equimolar responses. Results from air samples taken from dairy, poultry and swine operations allowed for the identification and quantification of hydrogen sulfide, carbonyl sulfide, carbon disulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, hydrogen sulfide and methanethiol.

Introduction

Volatile sulfur compounds (VSCs) are an important component of odor due to their low odor threshold values (Devos et al. 1990). These compounds have been identified as the dominant odorants emitted from both municipal sewage systems and pulp and paper mill facilities, and they are believed to contribute significantly to odor at animal feeding operations (AFO). Hydrogen sulfide is typically thought of as the main offender in terms of odor, but recent work by Willig et al. (2004 and 2005) suggest that methanethiol may also add significantly to the overall air quality. The extent to which VSCs in general contribute to odor is largely unknown since sampling and analysis of these compounds is challenging due to their volatility (Wardencki, 1998), reactivity (Wardencki, 1998; Bandosz, 2002; and Bentley and Chasteen, 2004.), sorption to surfaces (Kuster and Golden, 1987; and Sulyok et al., 2002) and low concentrations in ambient air (Wardencki, 1998).

Current monitoring of VSCs from AFO is relegated to the monitoring of hydrogen sulfide levels. The instruments used for this purpose measure hydrogen sulfide indirectly based on the conversion of hydrogen sulfide to sulfur dioxide and subsequent quantitation of sulfur dioxide (Summer et al., 2005a; and Summer et al., 2005b). However, recent work has shown that interferences from other VSCs may result in an overestimation of hydrogen sulfide levels in ambient air (Summer et al., 2005a; and Summer et al., 2005b). This highlights the need for a method that accurately quantifies all VSCs when monitoring air quality at AFO. Methods need to be developed that are robust enough to handle typical environmental conditions at AFOs (i.e., warm humid and dusty), while at the same time being able to speciate and quantify VSCs in ambient air.

Current field sampling and analysis are either unable to handle the demands of the AFO environment or do not lend themselves to sampling at AFO due to the complexity of the sampling (i.e., use of cryogen trapping). Tedlar bags sampling have been shown to be effective holding VSCs (Sulyok et al., 2001); however, in humid environments, this technique has been shown to sorb VSCs (Kuster and Golden, 1987). Drying of air has been shown to improve results with Tedlar bags; however, regardless of drying in-coming air hydrogen sulfide is still not possible (Nielsen and Jonsson, 2002).

Stainless steel canisters were found unsuitable for sampling VSCs (Parmar et al., 1996), but recent developments with FSL canisters have shown marked improvements in both recovery and storage stability of VSCs (Parmar et al., 1996 and Sulyok et al., 2001). Recovery of VSCs in the sub-ppb levels were possible even in high relative humidity environments (>95%) (Ochiai et al., 2001); however, stability of

VSCs stored in moist FSL canisters is less than three days (Ochiai et al., 2002). The stability of hydrogen sulfide in glass containers is strongly dependent on water content since in the presence of oxygen quantitative recovery of hydrogen sulfide was possible even after 120 hours (Devai and DeLaune, 1994). This is supported by the finding that removal of water from the sample stream with silica gel has extended the stability of VSCs in glass canisters (Casteel et al., 2006). The purpose of this paper is to provide information and discussion on a new technique using a FSL canister system for sampling and analysis of VSCs. The canister system uses heated robotic autosampler for improved transferring of canister contents to a preconcentrator that is subsequently analyzed on a GC/MS/PFPD. Parallel detectors on the GC system allowed for analysis of VSCs from the sub-ppbv to ppmv levels.

Materials and Methods

Chemicals and preparation of standard gases: Dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide and 1-propanthiol were purchased from Sigma-Aldrich (St. Louis, MO) at greater than 98%. These standards were prepared at 100 ppbv each in a fused silica lined (FSL) canister with zero grade nitrogen. EPA compliance grade standard gases made up in oxygen free nitrogen were purchased from Scott Specialty Gases (Plumsteadville, PA) and included carbonyl sulfide, sulfur dioxide, dimethyl sulfide, methyl mercaptan, and carbon disulfide all at 495 ppmv and hydrogen sulfide at 5 and 100 ppmv.

Reference gases were mixed and diluted using a dynamic dilution system (Entech Instruments, Inc., Simi Valley, CA). Final gas concentrations ranged from 10 ppbv for higher gas standards to 0.1 ppbv for hydrogen sulfide in nitrogen at varying RH. Stainless steel surfaces in the dynamic diluter manifold were coated with fused silica to minimize sorption of gases. Target compounds are listed with molecular weight, odor threshold, vapor pressure at 25°C (1 atm), Henry's law constants (mol atm^{-1}) in Table 1.

Sample Collection: Field samples were collected in 1.4 L FSL canister purchased from Entech. Samples were collected by either filtered quick fill (grab samples) or time integrated samples (2 hours) using restriction samplers. All surfaces on quick connects and restriction samplers were coated with sulfur inert fused silica. All samples were analyzed within one day of collection.

Analytical: Analysis of 1.4 L FSL canisters was performed using a model 7500 robotic autosampler (Entech Instruments, Inc.) connected to a pre-concentrator (7100, Entech Instruments, Inc.) that transferred into an Agilent 6890 (Agilent Technologies, Inc., Wilmington, DE). Transfer lines were fused silica lined tubing set at 150°C. The 6890 GC was equipped with GS-Gaspro column (30m x 0.32mm x 0.25um) (J&W, Wilmington, DE) using helium gas at 0.5 mL min⁻¹ constant flow, and equipped with both 5973 Inert MSD (Agilent Technologies) and PFPD (OI Analytical, College Station, TX) connected in parallel. The column effluent was split using an Agilent microfluidic plate prior to the MSD/PFPD detectors at an approximate 20:1 ratio.

The GC oven temperature program was: initial temp, 40°C; final temp., 260°C; initial time, 1.0 min; final time, 17.0 min; and ramp 20°C min⁻¹. The MS transfer line and source temperatures were 240 and 150°C, respectively. Mass spectrometer was operated in scan mode with the electron ionization (electron accelerating voltage: 70 V). The scan was set from m/z 24 to 300 in 0.7 s. For determination of the target compounds using MSD, selected ion chromatograms over molecular ions (hydrogen sulfide: 34 m/z; methanethiol: 48 m/z, sulfur dioxide: 64 m/z, carbonyl sulfide: 60 m/z, carbon disulfide; 76 m/z; dimethyl sulfide: 62 m/z, dimethyl disulfide: 94 m/z, dimethyl trisulfide: 126 m/z and 1-propanthiol; 94 m/z) were used. The PFPD detector was set at 200°C, 2 mm combustor tube, detector voltage at 600 V, detector gate delay at 6 ms, gate width at 24 ms, and detector trigger at 400 mV. The gas flows to the detector were at 12 mL min⁻¹ hydrogen, 11 mL min⁻¹ air, 12 mL min⁻¹ helium.

Table 1. Target Compound List

Compound	MW	Boiling Point	Vapor Pressure	QI	Odor Threshold
		(C)	(bar at 20°C)	(m/z)	ppbv
Hydrogen sulfide	34	-59.6	18.4	34	17.8
Carbonyl Sulfide	60	-50.0	10.1	60	55.0
Carbon Disulfide	76	115.0	0.53	76	95.5
Methyl Mercaptan	48	6.8	2.05	48	1.1
Dimethyl sulfide	62	38.0	0.45	94	2.2
Dimethyl disulfide	94	117.0	0.03	94	12.3
Dimethyl trisulfide	126	41.0	0.008	126	1.7

Results and Discussion

Detector Response Table 2 is a list of response factors, associated with different VSCs using the PFPD and MSD. The response factor for each VSCs was not an equal molar as expected with hydrogen sulfide having a higher response factor than any of the other gases tested. This was unexpected since Kim et al. (2005) demonstrated an equal molar response for all S compounds in his test system to be with 6% relative standard deviation (RSD). In this study, it should be pointed out that all gases except hydrogen sulfide gave equal molar response to sulfur within 9% RSD. In our study, the difference in terms of response factors between hydrogen sulfide and the other VSCs may due to dilution levels needed to equate hydrogen sulfide gas cylinder levels to the other VSCs gas cylinders. Kim (2005a and 2005b) showed that different sample introduction procedures will affect the respond factor for S using PFPD, and the more reactive the sulfur compound the lower the response.

Limit of Quantitation (LOQ) The LOQ for hydrogen sulfide on the PFPD was 0.23 ppbv; however, it should be kept in mind that our GC effluent split was set at 20:1 making our theoretical limit of quantitation set at 0.012 ppbv. The LOQ for sulfur compounds using the PFPD is well above typical odor thresholds for most VSCs (Devos et al., 1990). The dynamic range for sulfur compounds ranged from 0.23-400 ppbv sulfur with the PFPD. MSD inert source LOQ for hydrogen sulfide was determined to be 0.08 ppbv.

Storage Stability Storage stability of hydrogen sulfide was tested under both dry and wet conditions. The stability of hydrogen sulfide stored under dry conditions was over 1 week with greater than 90% recovered following three days of storage. However, storage stability of

hydrogen sulfide in moist air (relative humidity of more than 90%) was less than one week with only 74% recovered after 3 days.

Table 2. Response Factors for Select VSCs

Compound	PFPD		MSD Inert	
	Response Factor (pmol S/area)	r ²	Response Factor (pmol S/area)	r ²
Hydrogen sulfide	3.12 x 10 ⁴	0.984	9.13 x 10 ¹	0.999
Carbonyl Sulfide	2.51 x 10 ⁴	0.994	1.54 x 10 ²	0.997
Methyl Mercaptan	2.20 x 10 ⁴	0.991	1.14 x 10 ²	0.993
Carbon Disulfide	4.23 x 10 ⁴	0.967	1.52 x 10 ³	0.998

Table 3. Determination of VSCs concentration in air at AFO

Producer Facility	Location	H ₂ S ^a	COS ^b	Carbon Disulfide	Methyl Mercaptan	DMS ^c	DMDS ^d	DMTS ^e
Swine	Lagoon	4.8	0.6	2.5	ND ^f	0.95	0.14	ND
	Lagoon	36.5	8.3	27.8	ND	0.15	0.47	ND
	Manure Vat	10.5	15.5	13.1	55.0	83.1	81.5	22.7
	Manure Vat	6.4	10.7	2.4	7.6	88.6	162.7	<LOQ
Poultry (Broilers)	Exhaust	2.3	ND	1.7	2.0	4.3	14	0.6
	Tunnel							
	Brood Center	1.2	ND	1.2	2.6	2.5	11.3	<LOQ
Dairy	Cows	2.8	12.8	31.9	ND	<LOQ ^g	<LOQ	ND
	Manure	2.4	ND	62.3	ND	0.4	ND	ND

^aH₂S, hydrogen sulfide; ^bCOS, carbonyl sulfide; ^cDMS dimethyl sulfide; ^dDMDS, dimethyl disulfide; ^eDMTS, dimethyl trisulfide; ^fND, no detection; and ^g<LOQ, below limit of quantitation

Animal Operations: Table 3 is list of VSCs detected at swine, poultry, and dairy operations. This table clearly shows differences in the pattern of VSCs between animal production units and differences where samples are taken (i.e., inside building or outside building) in the ambient air. The main sulfur odorants near a lagoon appear to be hydrogen sulfide, carbonyl sulfide and carbon disulfide. It is hard to compare gauge data since little work has been conducted on the speciation of sulfur gases from swine facilities. The dominate sulfur odorants inside swine facility would include methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide. The dominate VSCs detected outside and inside a broiler house were dimethyl disulfide, which is different than what Chavez et al. (2004) found in poultry excreta. Chavez et al. (2004) found hydrogen sulfide and carbonyl sulfide as the dominate sulfur compounds in broilers. The dominate VSCs found in dairy operations were carbon disulfide and carbonyl sulfide. Previous studies monitoring air quality around have not reported detection of any volatile sulfur compounds (Sonesson et al., 2001; Rabaud et al., 2002; and Rabaud et al., 2003). This study clearly demonstrates that VSCs are in greater abundance at AFO than previously reported.

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Workshop on Agricultural Air Quality

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Methodology for Measuring Gaseous Emissions from Agricultural Buildings, Manure, and Soil Surfaces

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Abstract

Agricultural operations are one source of unwelcome and harmful gaseous emissions. Research is asked to determine emissions, to classify substance cycles as well as to elaborate and assess strategies for emission reduction.

Different emissions from agricultural operations have been investigated at the Leibniz-Institute for Agricultural Engineering Potsdam-Bornim (ATB) during the last years. Several methods are being applied and advanced. Pros and cons of the methods under study as well as special problems and advancements are discussed for investigations measuring gaseous emissions such as ammonia (NH_3), nitrous oxide (N_2O), methane (CH_4) and carbon dioxide (CO_2) from livestock buildings, manure storage facilities on laboratory scale and soil surfaces.

Introduction

Gaseous emissions from agricultural operations can mean both, the loss of nutrients and stress to neighbors and environment. The first step should be the determination of emissions. Secondly, emissions should be fit into the respective substance cycles, and consequences should be ascertained. On that basis abatement techniques can be investigated and assessed.

International notes and regulations aim at the reduction of ammonia (NH_3) as well as green house gas emissions (UN/ECE, 1999; EU, 2001). Animal husbandry is the main anthropogenic source for NH_3 (Berg et al., 2003) and emits also methane (CH_4) at a large extent (Mikaloff Fletcher et al., 2004). Soil generally can be considered as a sink for CH_4 , but on the other hand it is a source of nitrous oxide (N_2O) (IPCC, 2001). This study reports on methods to measure gas fluxes during agricultural operations on different scales (Fig. 1). The objective is to find out the most appropriate method for each agricultural operation in order to assess emissions and to advance abatement techniques.

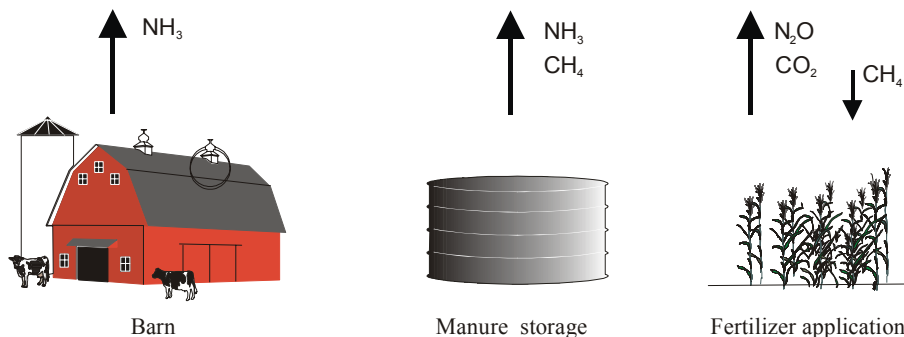


Figure 1. Main gas fluxes during agricultural operations

Methodology

Measuring System for Buildings

Gaseous emissions from forced ventilated buildings (poultry, pigs) (Fig. 2) as well as natural ventilated buildings (cattle) are measured by analyzing gas concentrations and determining the corresponding ventilation rates. Gas concentrations are analyzed by a photoacoustic multigas monitor. Special attention has to be turned to the influence of long tubes, different gas concentrations at sequent sampling points and low gas concentrations, near the lower detection limit. Ventilation rates are determined by 3 different methods: A) calibrated ventilation fans, B) CO₂ - balance method and C) tracer gases (SF₆ or Krypton 85).



Figure 2. Equipment for gas analyses and gravimetric tracergas dosing in a forced ventilated poultry house

The emission stream depends on gas concentration and ventilation rate. In both there are methodical aspects relating the results. Figure 3 gives an example for different gas concentrations at different fans which have identical air stream rates measured by measuring fans. There may be an influence of the length of the tubes because the distance from gas monitor to fan 9 was approximately 90 m. A conclusion is to have a few measuring points in a larger stable if the fans are running synchronized and to have a sampling point at each fan if the r.p.m. of the fans are controlled individually.

Table 1 includes results of the calculation of ammonia emission streams using different balance methods for determining the ventilation rate. These results give an impression on the influence of the ventilation rate and their accuracy. Both methods have their own difficulties. For example: SF₆ is a heavy gas with different distribution behaviour compared with gases like ammonia, especially under conditions with low air velocity. Carbon dioxide production data by animals are rather old (progress in breeding and increased metabolism) and mainly only available as averaged data of a day. So it is important to validate animal data under recent production conditions. Additionally there is more information necessary about the carbon dioxide release from litter and heating system. After that carbon dioxide balance method can be used as a non expensive method for calculation the ventilation rate in forced as well as in naturally ventilated farm buildings.

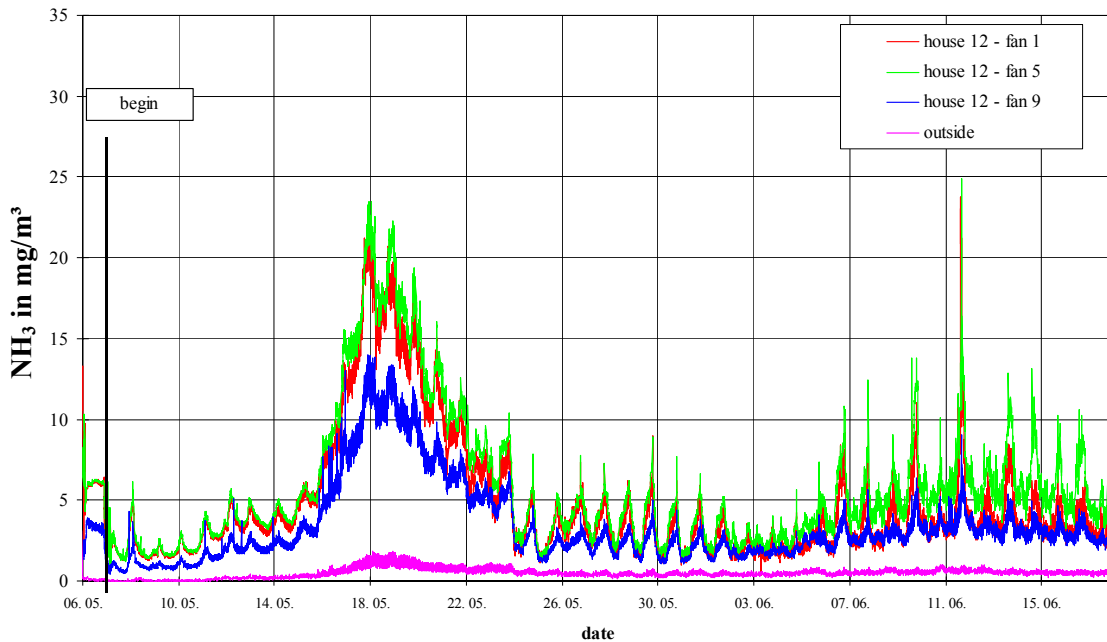


Figure 3. Ammonia concentration in exhaust air at different fans (springtime fattening period of chickens)

Table 1: Ammonium emission stream (g/year per laying hen) determined by SF₆ – and CO₂ – balance

	SF ₆ balance	CO ₂ balance
Winter	142.81	98.31
Summer	163.71	143.01

Measuring System for Storage Facilities on Lab Scale

Investigations on gaseous emissions from manure storage facilities were done in the emission measurement laboratory of the Leibniz-Institute for Agricultural Engineering Potsdam-Bornim (ATB) (Fig. 4). The room temperature of the lab was controlled and set to 20 °C. During first studies, room and manure temperatures were measured continuously. Since manure temperatures corresponded good to room temperatures, in the following only room temperature was recorded representing manure temperature too.

Between 50 and 75 kg manure were stored in cylindric vessels for periods of up to 200 days. Twelve vessels made of plexiglas[®] were used. Vessel volume amounted 92.4 l (diameter and height 0.49 m respectively).

Gaseous emissions were determined by using the open / dynamic chamber method. Vessels were closed and ventilated only during the measurements of the gaseous emissions with lids provided with air inlet and outlet. A compressor supplied the air inlets with fresh air. The fresh air flow rates were adjusted by air flow meters so that the air in the headspace was changed always one time per minute.



Figure 4. Measurement of gaseous emissions from manure storage facilities with dynamic chambers on lab scale

The headspace concentrations of the gases were determined by sampling exhaust air from each of the twelve vessels and analyzing by a photoacoustic IR analyzer (multigas monitor). Ammonia (NH_3), nitrous oxide (N_2O), methane (CH_4), carbon dioxide (CO_2) and water vapor (H_2O) concentrations were measured in the headspace and in the fresh air. Headspace concentrations of the different vessels fresh air (background) concentrations deducted were compared with each other and the control respectively. The gas fluxes calculated from the concentrations could not be used for calculating fluxes from on-farm storage facilities without further procedure. The different environment and volume to surface ratio of the vessels in the lab and on farms cause different gas fluxes.

The procedure of the measurement of the gaseous concentrations was the following: Exhaust air from each of the twelve vessels headspace and fresh air were sampled sequentially at 20 minutes intervals. The first 16 minutes vessel exhaust air and the last 4 minutes fresh air was sampled. The photoacoustic IR analyzer needed 2 minutes for analyzing one sample. Thus 8 values for exhaust air were generated per vessel and 2 values for fresh air between each vessel. The first 5 values from vessel exhaust air were used for stabilization and the last 3 values for calculating a mean value representative for the measurement. Fresh air between the vessels flushed the measuring chamber of the analyzer and demarcated measurements between each vessel. Fresh air concentrations were determined before and after the measurements of the first and the last vessel respectively. Figure 5 gives an example for the course of the NH_3 concentration of 2 vessels during a measurement.

Further parameters were determined:

- dry matter (DM), organic dry matter (oDM), total Kjeldahl nitrogen (TKN), total ammoniacal nitrogen (TAN), organic acids and conductivity of the manure by chemical analysis at the beginning and the end of the investigation period at least
- pH value of the manure, for liquid manure about 1 cm below the surface and 1 cm above the base (in the manure sediment) of the vessel
- odor concentration by an olfactometer
- sedimentation rate
- flow properties of the liquid manure by a rotational-type viscometer.

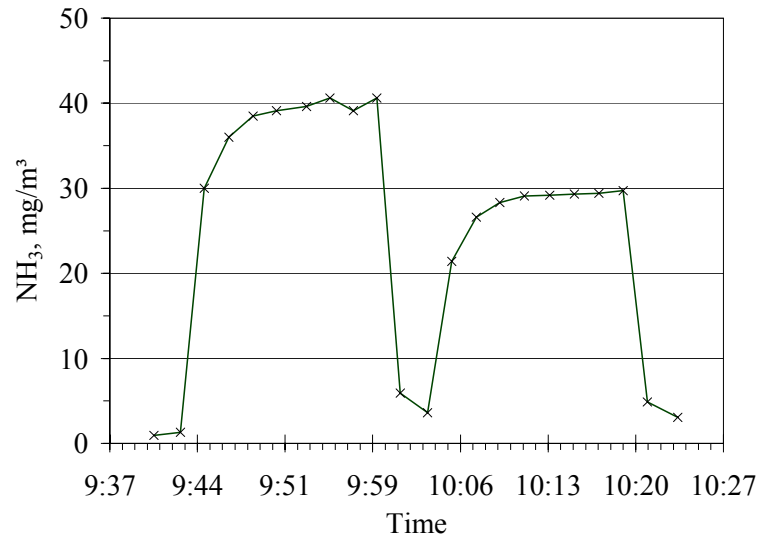


Figure 5. Increase of NH₃ in dynamic chambers for manure storage.

Measuring System for Field Application – Gas Fluxes from Farm Manure Composting

Measurements of emissions of CO₂, CH₄, N₂O and NH₃ are performed at a biological operating farm. The animal waste from cattle and pigs is composted continuously in a so-called layer system ("sandwich composting"). After composting, the material is stored and utilized correspondingly. The windrows of animal waste (straw bedding with cattle manure and pig manure) are arranged in parallel trapezoidal rows of about 40 m length, 4 m width and up to 1.2 m height (Fig. 6).



Figure 6. Measurement of linearity of concentration increase of a gas flux chamber on windrows of animal waste (straw bedding with cattle manure and pig manure) by a multigas monitor

Gas samples from composting are gained by collection in gas flux chambers (volume 0.189 m³ and area 0.292 m²; Fig. 6) and sample gasbags, each with 10 l volume, after a specific time. At the beginning of the studies, the linearity of the concentration change in the gas flux chambers on dung was analyzed (Fig 7). The increase of CO₂ concentration was used as a reference. The results showed that a linear approximation could be applied over a period of at least 10 min.

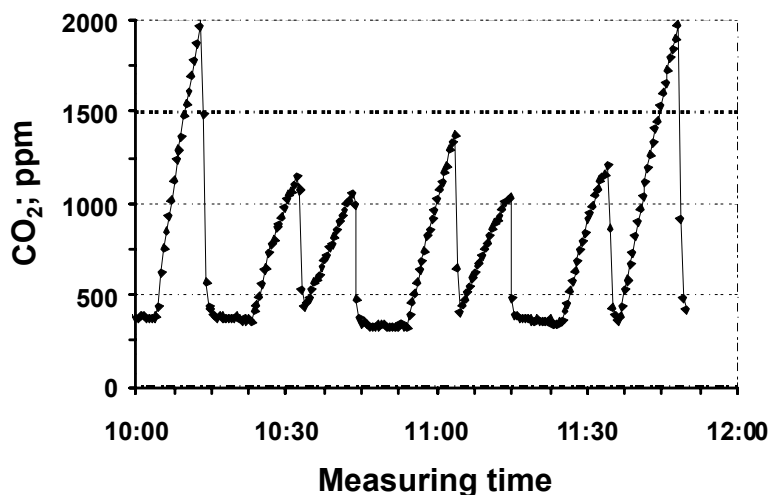


Figure 7. Increase of CO₂ in a gas flux chamber on windrows of animal waste, measured with multigas monitor

The trace gas analysis was made by means of a high resolution FT-IR spectrometer. To achieve sufficient sensitivity for quantitative FT-IR detection, a heated measuring cell (80 °C, measuring volume 5 l) with an optical path length of 20 m was utilized in combination with an HgCdTe-detector (MCT). The measuring cell and all pipes were evacuated before each measurement. The systematic error in the determination of concentrations was estimated to be about 20% for the determination of CH₄, CO₂ and N₂O. The accuracy of the measurement depends on the type of gas and the concentration span to be evaluated (line positions and changes in line intensities), on calibration and spectrum evaluation, and on measurement procedures.

The relative error of NH₃-measurements doubles approximately for low concentrations (below 5 ppm) due to the high mobility and extraordinary absorbability and diffusion of NH₃ molecules, even through solid materials. The time period between gas collecting and gas analysis led to additional systematic and stochastic errors. To reduce this type of systematic error, the concentration change as a function of the storage time in gasbags was tested. By regression analysis, a mean decay function $C(t) = C_0 (1 - b \cdot t)$ was obtained. For CH₄ and CO₂ the coefficient b is 0.0039 h⁻¹ and for N₂O and NH₃ b is 0.0086 h⁻¹. After a storage time of 6 hours (or up to 24 hours), the concentration of CH₄ and CO₂ dropped by about 2.5% (approx. 10% after 24 h) and in case of N₂O and NH₃ this decay was approximately 5% (approx. 20% after 24 h). Stochastic errors of the FT-IR-measurements of ambient air, caused by electronic noise and temperature drifts of the interferometer, were estimated to be in the range of 5%. The stochastic error due to gas sampling by flux chambers on dung windrows further reduced the accuracy in the determination of emission rates during composting of farm waste.

The FT-IR spectrometer used here operates as a so-called one-beam system. To get a pure sample spectrum, at first the background spectrum (empty gas cell) must be measured. Then the sample spectrum is get by a second measurement with filled gas cell and evaluating the changes in relation to the background. For minimizing of stochastic and systematic errors, the background must have at least the same quality (signal to noise ratio) as the sample spectrum. Additionally it is necessary to stabilize all spectrometer conditions. Therefore, the FT-IR spectrometer with its beam channels and detector housings was purged by dry and CO₂ free air (FT-IR Purge Gas Generator; -73°C dew point of cleaned air). Usually spectra were recorded with 64 scans. Accumulation improves the signal to noise ratio, and such a way the accuracy of concentration determination.

FT-IR Calibration and Concentration Measurements

Spectrum Quant+ (PERKIN ELMER software) was applied for concentration evaluation of the FT-IR spectra. The software operates with chemometric procedures (PLS: partial least-squares) based upon inputs from calibration spectra. This multi regression method was developed by Wold (1966). A cross-validation was used. For base line corrections, first derivatives were chosen. The spectra had to contain the range of gas concentrations of the gas (or gases) to be evaluated and, if possible, different concentration levels of disturbing gases like water vapor or others. Secondly, during the development of the calibration method, the most suitable wave number ranges for the calibration procedure had to be put in, or in other words, non-interesting and disturbing spectrum regions were to be “blanked”. In the calibration methods, developed here, 15 to 30 standards (calibration spectra) were measured with a resolution of 0.2 cm^{-1} and a point interval of 0.05 cm^{-1} .

For multi gas analysis, the concentration distribution with the maximum of mutual linear independency was calculated. Then, specific instrument calibration mixtures (Linde HiQ[®] Specialty Gas) were applied or, in most of the cases, the gas mixtures were produced by using volume calibrated 10 dm^3 plastic bags (Linde Plastigas[®]; Linde, 2006) filled with nitrogen or filled with ambient air of known composition and adding definite quantities of pure gases by micro-liter syringes through the septum of the bags. It was found that the best calibration methods were achieved using the PLS1 algorithm of the software and blanking all spectra parts except regions with no or only weak overlapping spectral lines. These lines were determined by qualitative measurements with variable concentrations and by spectra simulation using USF-HITRAN-PC (HITRAN, 1992). It was found that the best accuracy could be achieved when the standard lines and sample lines did not differ in the magnitude of absorbance. Although it is possible to develop a calibration method, which works for e.g. CO_2 from 200 ppm till 20% by volume, usually strong deviations between predictions and real concentrations will be measured in the low or high edge of the concentration range. Therefore, for evaluation of high variable gas concentrations in the sample, e.g. from compost air, intensity adopted calibration software tools had to be applied.

Measuring System for Field Application – Flux Rates from Soil

The closed chamber technique is applied on an experimental field in order to obtain the seasonal and the spatial variability of N_2O and CH_4 soil fluxes. Gas flux measurements are performed several times weekly by means of an automated gas chromatograph (GC). The gas flux chambers are placed for the measurements at sealing rings (Y profile, sealing by water level) embedded in the soil. The gas flux chambers have a volume (V) to area (A) ratio of $V/A = 0.315 \text{ m}$ (volume 0.064 m^3 , inner diameter 0.509 m). Two evacuated gas samplers (100 cm^3 bottles with Teflon sealing and vacuum taps) are connected to each box. The first is filled when the box is put on the water-sealed ring on the soil and the second one after about 60 minutes enclosure time. Then the samplers are connected with the automated GC-injection control system. The GC is fitted with an electron capture detector (ECD) and a flame ionization detector (FID). The operating temperatures for the ECD and the column temperature are $300 \text{ }^\circ\text{C}$ and $65 \text{ }^\circ\text{C}$ respectively. Both the pre-column (length 1 m) and the main column (length 3 m) are packed with Porapak Q (80/100 mesh). In one computer-controlled run up to 64 samples can be analyzed.

To apply a two point evaluation for gas flux measurements, the linearity of the concentration increase and the concentration gradient inside the gas flux chamber must be known. CO_2 and N_2O , both of them generated in the soil, have nearly equal diffusion constants. The easily measurable CO_2 served for the evaluation of linearity and mixing homogeneity of the measuring chamber (measurements at several heights in the closed chamber). Studies on the concentration increase of CO_2 in a flux chamber on bare soil and on grass sites demonstrated that the increase in concentration was linear (R^2 between 0.9973 and 0.9986) during measurement periods of 60 minutes (Fig. 8).

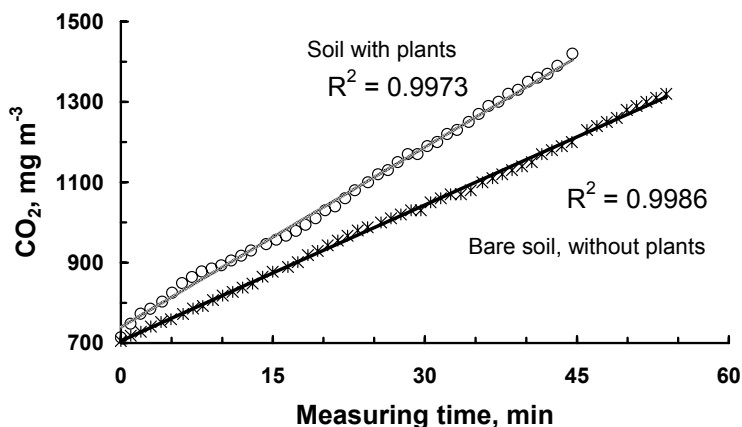


Figure 8. Increase of CO₂ in a gas flux chamber on bare soil and on soil with plants

Conclusions

Different emissions from agricultural operations have been investigated at the Leibniz-Institute for Agricultural Engineering Potsdam-Bornim (ATB) since several years. Gaseous emissions such as ammonia (NH₃), nitrous oxide (N₂O), methane (CH₄) and carbon dioxide (CO₂) were determined from livestock buildings on farms, manure storage facilities on laboratory scale, manure composting on farms and soils. Various methods were being applied and advanced for the special gases and emission sources.

The favored methodology for the determination of emissions from livestock buildings on farms was analyzing gas concentrations by a photoacoustic IR analyzer and ascertaining the corresponding ventilation rates. The ascertainment of the ventilation rates depended on the ventilation of the building. For forced ventilated buildings, it was ascertained by calibrated ventilation fans and for natural ventilated buildings by tracer gases (SF₆ or Krypton 85). For the investigation of emissions from manure storage facilities on laboratory scale, the open / dynamic chamber method was preferred. Gas concentrations were determined by a photoacoustic IR analyzer also used for building measurements. The closed chamber method was applied for measuring gas fluxes from farm manure composting and from soils. Gaseous emissions from manure composting (CH₄, CO₂, N₂O and NH₃) were determined by a high resolution FT-IR spectrometer. Emissions from soil (CH₄, CO₂ and N₂O) were measured with an automated gas chromatograph (GC) fitted with an electron capture detector (ECD) and a flame ionization detector (FID).

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A Methodology For Estimating Ammonia Emissions From Farm Manure Storage Using Passive Sampling and Atmospheric Dispersion Modeling

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Abstract

Ammonia emissions from stored farm manures form a small but significant proportion (~10%) of the total emitted annually from UK sources. These emissions are regulated by a number of factors including: the surface area of the store; the storage method; the physical form of the stored manure and the source of manure. A method was developed to estimate in-situ emissions from a range of store types in order to address the variability associated with these emissions. Passive diffusion samplers (Willem's Badges) were used to determine vertical concentration profiles to a height of 4.5 m at a number of locations around each slurry store. An atmospheric dispersion model was applied to estimate the contribution from emissions from other on-farm ammonia sources to the measured data and also to determine the emission rate from the stored manure. A procedure was applied whereby the emission rates from each source were allowed to vary and a numerical equation solver was applied to backfit the modelled data set to the field measurements.

This methodology was applied at four farms that used two types of stores (weeping wall and earth banked lagoon) that are currently under-represented in UK emissions estimates. This paper reports the emissions for one of the farms that operated a weeping wall lagoon, a system which allows the partial separation of slurry solids and liquids, which can then be managed more conveniently as separate components. These measurements were collected on a monthly basis for a complete year, with each dataset being collected over 24 hours. Emissions were found to peak at 2 g NH₃-N m⁻² day⁻¹ in spring, reducing considerably over the summer and winter periods. The average emission from the farm was 0.7 g NH₃-N m⁻² day⁻¹ which agrees with other recent data on ammonia emissions from crusted slurry stores and, though it is within the range of data considered in the UK emissions inventory, suggests that emissions from this type of store may be currently overestimated in national predictions.

Introduction

Emissions of ammonia (NH₃) to the atmosphere in the UK are dominated by the contribution from the agricultural sector (Pain et al., 1998). These emissions originate from the surface application of agricultural wastes, livestock housings, slurry stores, fertiliser applications and grazing. Such inventories are relied upon to determine the total emission from UK agriculture and are increasingly being used to develop abatement strategies for targeting reductions in NH₃ emissions and to demonstrate compliance with international legislation on NH₃ emission ceilings (EC, 2001). The accuracy of the emission estimates from these inventories is dependant on the quality of the emission factors that are applied. For some of the agricultural practices included within the inventories, emissions estimates are based on a limited number of field trials that may not fully reflect the real-world variability. In particular, prior to this study there were no direct measurements of emissions from weeping wall or earth-banked lagoons with strainer boxes, which together account for approximately 30% of dairy slurry storage (Smith et al., 2001). These stores provide partial separation of slurry solids and liquids, with one or more sides of the store having slatted walls allowing liquid to drain to a separate storage area. The liquid and semi-solid manure fractions can then be managed separately. There are three distinct potential areas of NH₃ emission: a) the storage surface; b) the wetted slatted walls and drainage channels; c) the liquid storage area surface, and these may result in different emission characteristics than for a conventional slurry lagoon.

The overall project objectives included the partitioning of nutrients between the solid and liquid phases of the stored manure, but in this component of the study the aim was to quantify NH₃ emissions from the

semi-solid and liquid storage fractions in weeping wall/strainer box lagoons. This paper describes the methodology developed to make such measurements and reports preliminary results for one of the study sites.

Estimation of Emission Fluxes

The dispersion of NH₃ emitted to the atmosphere can be determined at a farm-scale using mathematical models (Hill et al., 2001, Fowler et al., 1998). Such models are typically used to predict air concentrations and deposition fluxes arising from known, or estimated, rates of emission. However, these models can also be applied to back-calculate emission rates from known air concentrations.

Back-calculation techniques have been applied to determine emission rates from single isolated sources such as slurry applications (McInnes et al., 1985). For the sites that were investigated in this study NH₃ concentrations were likely to arise from a number of on-farm sources depending on the direction of the prevailing wind. Attempts were made to limit these influences during the site selection process, through the design of the field experiments and through conducting monitoring during periods when favourable wind directions were forecast.

A modified back-calculation method was developed that applied an advanced atmospheric dispersion model along with a multi-variant statistical modelling tool to both determine emission rates from the slurry stores and to account for emissions from other on-farm sources.

Measurement of Air Concentrations

Air concentrations were measured at several heights surrounding each slurry lagoon. This enabled the statistical model to diagnose emission fluxes from the measured horizontal and vertical distributions of air concentrations. Vertical concentration distributions have been found to vary strongly with source type. Ammonia emitted from stored manure is advected by the wind immediately upon release, hence the vertical concentration profiles are similar to those from an equivalent sized surface-level area source, with concentrations reducing rapidly with height. However, NH₃ initially emitted into a naturally ventilated farm building is relatively well mixed within the confines of the building, being released through both the sides and roof of the structure. The dispersing plume from farm buildings therefore lacks the strong vertical signal of a plume from a ground level source, with measurements showing such plumes are almost uniform with height below the roofline of the building (Hill et al., 2001).

Passive sampling methods based on diffusion theory are useful when simultaneous measurements are required at numerous spatial locations and at varying heights, as they are light and have no requirement for electricity. The Willems badge sampler (Willems, 1990) was applied in these field experiments as this sampler can measure air concentrations over 24 hour periods with a limit of detection between 1 –5 µg NH₃-N m⁻³, furthermore the sampler has a precision of the order of +/- 10 % (Hill, 2000).

Air concentrations (χ_a) are calculated, using Equation 1, from measurements of the mass of NH₃-N collected on the absorption filter (M_c) of the Willems badge minus a laboratory blank value (M_b), the combined boundary layer and filter resistance of the badge (R_b+R_f , 164 s m⁻¹ at 15 °C), the area of the filter (A , 6.158 x 10⁻⁰⁴ m²) and the duration of the experiment, t (in seconds).

$$\chi_a = \frac{(M_c - M_b) (R_b + R_f)}{A t} \quad \text{Equation 1}$$

Willems badges were mounted on a number of masts at each of the experimental sites at heights of 0.5 m, 1.0 m, 2.0 m, 3.0 m and 4.5 m.

Atmospheric Dispersion Modeling

Dispersion factors (D in s m⁻³) were calculated using the UK-ADMS atmospheric dispersion model. This model was chosen as it includes a realistic treatment of the physics of the atmospheric boundary layer, using Monin-Obukhov scaling, to describe the vertical variation in wind speed and turbulence in the atmosphere, and also as it incorporates a building effects module which allows for the streamline deflections and enhanced turbulence that occur downwind of animal housings.

The ADMS model was configured with the following input data:

- a) Meteorological data for each measurement period, including wind speed and wind direction at a specified height (typically 2 m), air temperature and solar radiation.
- b) Source location and dimensions for the major points of NH₃ emission at each of the farms, including the slurry lagoon, dirty water stores, the main buildings on the farm, open areas and feedlots.
- c) A building configuration at each of the farms.
- d) Estimates of the surface roughness length for the farm buildings and meteorological sites.
- e) The position of each of the Willems badge monitoring points.

Multi-Variant Statistical Model for the Determination of Emission Rates

For each of the NH₃ emission sources (i), dispersion factors were calculated for the complete array of Willems badge monitoring points (j). Modelled air concentrations could then be determined at each Willems badge monitoring point ($\chi_{m(j)}$) from known emission rates for each source ($E_{(i)}$, in $\mu\text{g NH}_3\text{-N s}^{-1}$) using Equation 2.

$$\chi_{m(j)} = \sum_i D_{(ij)} E_{(i)} \quad \text{Equation 2}$$

The level of agreement between the modelled and measured air concentrations can be determined using the Normalised Mean Squared Error (NMSE), a statistic applied in the ASTM methodology for model evaluation (Irwin et al., 2003). Equation 3 shows an implementation of the NMSE using the dispersion modelling methodology applied herein and accounting for a constant background concentration (χ_b). Overbars denote ensemble means.

$$NMSE = \frac{\overline{[\chi_{a(j)} - (\chi_{m(j)} + \chi_b)]^2}}{\chi_a (\chi_m + \chi_b)} \quad \text{Equation 3}$$

A numerical equation solver was used to determine the emission rates for each source ($E_{(i)}$) and overall background concentration (χ_b) that resulted in the minimal value of NMSE. This methodology was applied to each of the experimental runs. The initial values for $E_{(i)}$ were obtained using the emission factors contained in Misselbrook et al. (2000). As values of $E_{(i)}$ calculated using this methodology incorporated the data from all the measured air concentrations, replication of the Willems badges at a single height was not required.

Experimental Setups

Field experiments were conducted at four farms, two sites in Devon and locations in Wiltshire and Nottinghamshire. This paper reports the store characteristics and preliminary results for one of the Devon sites, a dairy farm with approximately 185 cows.

An aerial photograph of the farm is shown in Figure 1. A large rectangular weeping wall type slurry store (25m wide and 34 m long) can be seen adjacent to the main cubicle house. Slurry from the cubicle house was scraped daily into the store via a ramp at the NW corner. The S and E walls of the store were slatted, allowing liquid to drain from the store via channels to two smaller 'dirty water' lagoons (at the bottom of Figure 1) from where it could be irrigated directly to the land. In addition, dairy parlour washings and yard run-off were channelled directly to the dirty water lagoons. Measurements were made on three sides of the slurry lagoon, close to the dirty water store and in the fields to the south of the lagoon (to provide an estimate of background concentrations). Those measurements collected close to the slurry store would be relatively unaffected by emissions from the farm buildings for wind directions from the south and south-east, though strong contributions would be expected for winds from the north-west and west.

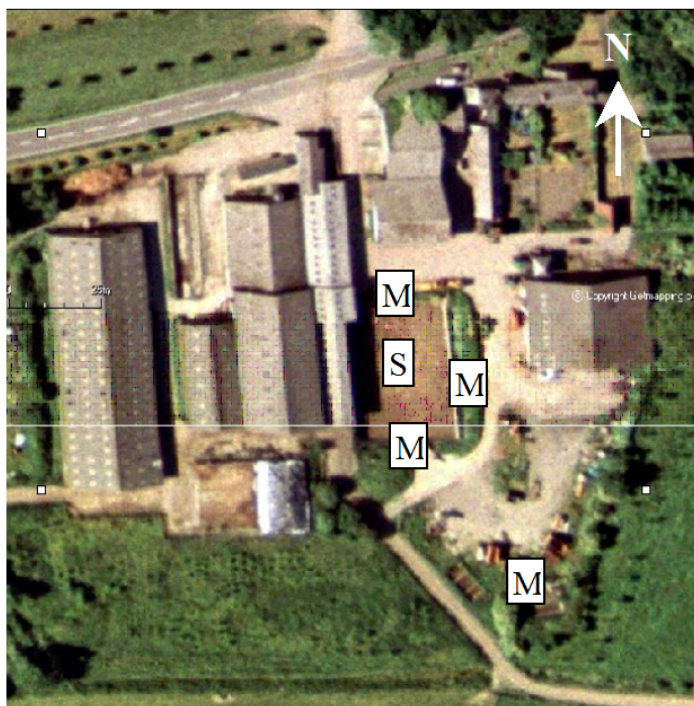


Figure 1. Aerial photograph of the study farm. The location of the slurry store is designated as (S), the locations of the on-farm measurement masts are designated as (M). A background mast was located in the fields to the south of the farm (not shown). Aerial photograph copyright Getmapping.com.

Results and Discussion

Meteorology

A summary of the meteorological data for the study farm is shown in Table 1. The meteorological data summary illustrates that a considerable variability in the wind directions often occurred over the duration of each of the measurement periods (shown by the standard deviation, sigma, of the wind direction). For many of the experimental runs, measured air concentrations could not be assumed to be only derived from emissions from the slurry store, confirming that the statistical methodology described previously was required in order to account for the influence of the additional on-farm NH_3 sources.

Table 1. Summary of meteorological measurements from the study farm. Data were collected at a 30 minute time resolution and a height of 2 m.

Start date	Duration (hours)	Wind speed (m s^{-1})		Wind direction (degrees)		Temp. ($^{\circ}\text{C}$)	RH (%)	Solar radiation (W m^{-2})		Rainfall (mm)
		Mean	Sigma	Mean	Sigma	Mean	Mean	Mean	Max	Total
12/09/02	24.0	1.9	1.6	86	70	15.2	88	125	524	1.0
24/10/02	24.0	2.5	1.6	214	74	11.8	90	64	293	4.0
03/12/02	25.5	1.6	1.4	347	92	7.8	92	27	151	4.8
15/01/03	23.5	1.9	1.6	260	51	4.6	93	27	214	0.0
26/02/03	23.5	3.2	0.9	122	7	7.9	91	17	134	0.2
15/04/03	21.5	1.2	1.1	152	77	12.1	74	162	730	0.0
16/06/03	26.0	1.5	1.1	217	68	15.9	80	285	826	0.0
24/07/03	26.0	2.0	1.1	206	91	15.6	92	135	816	24.8
12/11/03	27.0	1.4	1.2	250	97	8.6	92	45	313	0.0

Air Concentrations

The air concentrations measured during each of the experimental runs were used to diagnose the emission rates from the slurry store. This methodology was applied to the complete dataset of concentrations from each run and made use of the differences in the vertical concentration profiles from stored manure and from naturally ventilated farm buildings.

Vertical concentration profiles are shown in Figure 2 for a sampling mast where winds from the southwest (on 24-10-02) would include NH_3 concentrations from both the slurry store and the farm buildings, and from the southeast (on 26-02-03) where NH_3 concentrations would be predominantly derived from the slurry store. The profiles from 24-10-02 were interpreted using the atmospheric dispersion model showing that, at the lower sampling points in the profile, concentrations were mainly derived from the slurry store whilst at elevated points, to which emissions from the slurry store had not been vertically dispersed, NH_3 concentrations were derived from the farm buildings. The vertical concentration profile for 26-02-03 shows the situation where wind trajectories were unaffected by the farm buildings, hence the vertical concentration profile shows a classical exponential decrease with height, tending to background values at the upper measurement locations.

Emissions

Table 2 summarises the Normalised Mean Squared Error and Correlation squared (R^2) statistics from the multi-variant modelling approach used to derive emission rates from the measurements. These statistics are useful to illustrate the relative uncertainty that affected individual monitoring periods and show that for seven of the nine sampling runs, low values of NMSE (scatter between measured and modelled values) and R^2 values close to 0.9 were found illustrating accurate model estimates of emission rates.

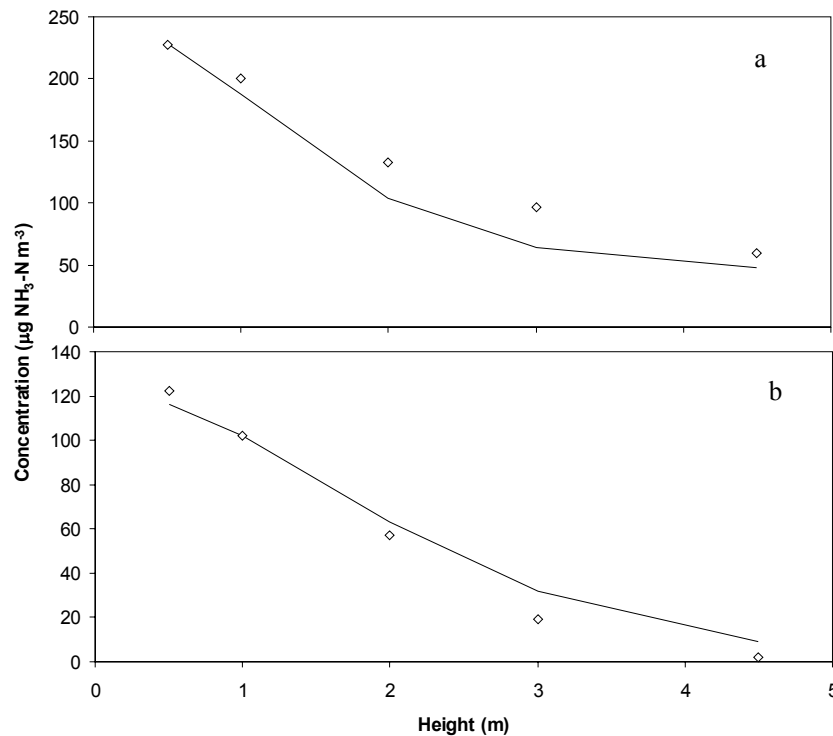


Figure 2. Air concentrations of $\text{NH}_3\text{-N}$ measured (points) and diagnosed using the atmospheric dispersion model (line) for the northerly mast shown in Figure 1 for 2 periods: (a) when wind trajectories included influences from the buildings (24/10/02); and (b) when wind trajectories were consistently from the slurry store (26/02/03).

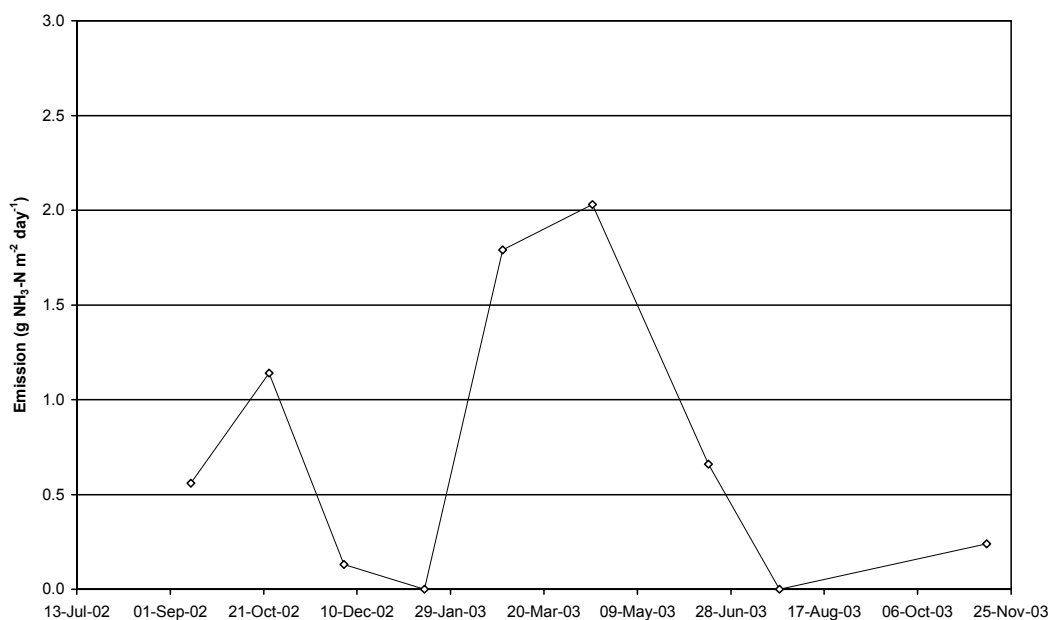
Table 3: Normalised Mean Squared Error and Correlation statistics determined following the multi-variant analysis used to diagnose emission rates from the slurry store.

Run	Date	NMSE	R ²
1	12/09/02	0.31	0.87
2	24/10/02	0.29	0.90
3	03/12/02	0.01	0.98
4	15/01/03	0.12	0.87
5	26/02/03	0.03	0.99
6	15/04/03	0.38	0.89
7	16/06/03	0.37	0.64
8	24/07/03	1.06	0.35
9	12/11/03	0.06	0.91

The timeseries of diagnosed emission rates (Figure 3) showed marked variations throughout the measurement period, with peak values of approximately 2 g NH₃-N m⁻² day⁻¹ occurring in spring. In contrast, a considerable reduction in emission rates was found over the winter and summer periods.

Using the data presented in Figure 3, an average emission rate from the slurry store was determined over the period of the measurements of 0.7 g NH₃-N m⁻² day⁻¹. This compares with a value of 2.17 g m⁻² day⁻¹ that is applied for crusted slurry stores in the UK Ammonia Emissions Inventory (Misselbrook et al., 2000), indicating that the contribution from weeping wall stores may be currently overestimated. It should be noted however that the emissions reported herein are within the range of data used by Misselbrook et al. (2000) to derive their emission estimate.

Similar results were determined for the other sites studied (not presented here), where average emission rates were found to range between 0.4 – 0.7 g m⁻² day⁻¹. Recent results from chamber studies have also reported similar emission rates from crusted slurry lagoons, with an average emission estimate of 0.5 g m⁻² day⁻¹ (Smith et al., 2004), illustrating the reproducibility of the data presented herein.

**Figure 3. Timeseries of NH₃-N emissions from the slurry store.**

Conclusions

A new in-situ method of deriving emission rates from farm waste stores, based on passive sampling of NH₃ concentrations in air and atmospheric dispersion modelling, was applied at four UK farms that used either weeping wall stores or earth banked lagoons with strainer boxes. The results from one of these farms that used a weeping wall store are reported herein. The measured air concentrations were found to be well described by a numerical modelling framework, with modelled vertical concentration profiles providing a good fit to the measured data both for the situation where air concentrations were derived from a single source (the slurry store) and where concentrations were combined from multiple on-farm sources (the slurry store and farm buildings). The diagnosed emission rates from the slurry store were found to vary throughout the year, with peak emissions occurring in spring of 2 g NH₃-N m⁻² day⁻¹. Emissions averaged over the year were 0.7 g NH₃-N m⁻² day⁻¹ which, whilst within the range of data compiled for the UK Ammonia Emission Inventory, suggests that emissions from weeping wall stores may be currently overestimated.

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