Proceedings

Workshop on Agricultural Air Quality: State of the Science

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Preface

Emissions of air pollutants during agricultural operations are an important emerging research area, best studied with interdisciplinary approaches that can inform policy makers of the costs and benefits of various potential mitigation options. Agriculture, forest, and range production practices are increasingly subject to U.S. State and federal regulations intended to protect air resources. However, data on agricultural emissions of regulated pollutants, nuisance odors and fugitive dust often either do not exist or are insufficient to develop appropriate policy, both in the United States and worldwide.

The First Workshop on Agricultural Air Quality: State of the Science was held in Potomac, MD, USA in 2006. The primary focus of the Workshop was on improving agricultural air quality inventories and recommendations for technological and methodological changes in current emissions measurement and modeling practices.

More than 300 scientists, engineers, resource managers, decision makers, and policy analysts attended the Workshop. The participants represented 15 nations from five continents. Their disciplines ranged from atmospheric chemistry to soil science. The participants represented many stakeholder groups concerned with the growing need to understand agricultural impacts on our atmosphere and to develop beneficial policies to improve air quality. Attendees included leaders in international, federal, state, and local government; academia; environmental and public interest groups; business leaders in crop and animal agriculture; and professional societies and trade associations.

Policy issues and advancements in the sciences associated with agricultural air quality were explored and summarized in several forums and formats during and after the Workshop. This volume represents the formal workshop proceedings; summary and synthesis papers will follow in several leading journals.

We hope that this workshop will be only the first of several that will bring the issues of agricultural air quality to greater public visibility and scientific understanding. As we rise to the challenge of feeding more than 6 billion fellow citizens of the world, the ancillary impacts of our food production systems will become more widespread and severe. We must not forget the importance of good air quality, even as we may succeed wondrously in our agricultural production.

Viney P. Aneja
William H. Schlesinger

Workshop Co-Chairs

Foreword

The "Workshop on Agricultural Air Quality: State of the Science" represents a significant milestone for air quality research and technology transfer at the United States Department of Agriculture (USDA). Until several years ago, research on air quality at USDA and its partner institutions was a very loose collection of projects scattered about the country with very little programmatic institutional support. Environmental concerns and increasing regulatory pressures on agriculture related to air quality led to the formation of the USDA Agricultural Air Quality Taskforce (AAQTF) in 1996. The AAQTF provided recommendations to the Secretary of Agriculture regarding priority research areas. The AAQTF also recommended the allocation of more resources to air quality research. These recommendations, coupled with increased awareness by the land-grant university community, have resulted in steadily increasing resources for agricultural air quality research and extension. Resources have grown almost ten-fold in the past decade, from $2-3 million per year in 1996 to approximately $20 million per year in 2006.

One of the most significant increases came in 2003 when the USDA National Research Initiative (NRI), administered by the Cooperative State Research, Education and Extension Service (CSREES) created a new $5 million per year air quality research program. The NRI Air Quality program seeks to provide sound science that protects the environment while maintaining a viable agricultural production system. This is primarily a research program that focuses on developing quantitative emissions data for agricultural production practices and improving information about the measurement, control, fate, and transport of odor, gases, and particulate matter. This program also includes research on emissions and means of reducing greenhouse gases (GHGs), such as nitrous oxide and methane. In addition to research, the NRI Air Quality program engages in outreach activities that include transferring technologies and best practices to producers and the regulatory community to lessen the production and transport of air pollutants and greenhouse gases. In its third year of funding, the NRI Air Quality Program has funded a cumulative total of $15.4 million in research and outreach activities.

As part of the post award management strategy of the NRI Air Quality Program, a workshop was solicited as part of the 2004 request for applications. The solicitation asked for some very specific outputs from the Workshop. First, a pressing need for U.S. agriculture is to update and add to the emissions inventory for agricultural production practices. Second, a catalogue of best practices for reducing and mitigating agricultural emissions is needed. These two needs represent two of the emphasis areas in the NRI solicitation and have received substantial research investments. One of the primary goals of this Workshop is to bring together the science and experiences from researchers and stakeholders to produce these two documents. Participants in the Workshop will play a critical role in providing data, technologies and practices, and review of these documents.

Developing sound research needed for agriculture in an increasingly regulated environment is a particularly challenging opportunity. The immediacy of policy and laws to protect people and resources contrasts with the much slower process of problem solving based on hypothesis testing and technology transfer. The unique mission of the CSREES Air Quality Program — to foster sound science, enhance stakeholder education and competencies, and transfer this knowledge through high-impact extension programs — is critical in developing effective agricultural air quality policies. Participation in and the resulting outputs from this Workshop will provide the research and outreach necessary to assist regulatory authorities in developing and implementing appropriate, scientifically-based permit options for agricultural producers based on high quality peer-reviewed emission data. Practices documented at this Workshop should enable the development and evaluation of emission control technologies that are both effective and economical for producers.

Raymond E. Knighton

National Program Leader – Air Quality
USDA-CSREES

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- North Carolina State University
- North Carolina Water Resources Research Institute
- Phosphate and Potash Institute, The Fertilizer Institute
- United States Department of Agriculture, Agricultural Research Service
- United States Environmental Protection Agency

The workshop was planned over a 2-year period. During that time the five members of the **Steering Committee** (Dr. Cliff Duke, Dr. Greg Jennings, Dr. Ray Knighton, Dr. Dev Niyogi, and Dr. Wendell Gilliam), and the 19 members of the **International Executive Scientific Advisory Committee** (Dr. John D. Bachmann, Prof. A.F. Bouwman, Prof. Guy Brasseur, Prof. Candis S. Claiborn, Dr. O.T. Denmead, Dr. Jan Willem Erisman, Dr. Paul A. Fixen, Prof. David Fowler, Prof. Deug-Soo Kim, Mr. Bruce Knight, Dr. Raymond Knighton, Prof. Menachem Luria, Dr. Soeren Pedersen, Dr. Major Paul A. Roelle, Prof. Mukesh Sharma, Dr. Hanwant B. Singh, Dr. J. Webb, Dr. Steven Whalen, and Dean Johnny Wynne) worked diligently with the Workshop Co-Chairs (Prof. Viney P. Aneja and Prof. William H. Schlesinger) to ensure that the Workshop was a success.

We appreciate the efforts of the publishers involved with the publishing of the Proceedings, namely North Carolina State University; the U.S. Department of Agriculture; and Mr. David Caldwell, who oversaw the publication. We would like to thank Ms. Jessica Blunden, who assisted during this process.

We are appreciative of the staff at the Beltsville Agricultural Research Center and at the Goddard Space Flight Center for hosting, organizing, and delivering the technical presentations for the science tour and field trip.

We thank the staff of the Bolger Center in Potomac, MD, for providing a state of the art conference center and assistance with administrative details.

Lastly, we would also like to thank the staff of the Ecological Society of America, particularly Bette Stallman, Tricia Crocker, and Rhonda Kranz, for all of the hard work and creative planning necessary to bring a Workshop of this magnitude together. The Workshop could not have been successful without their efforts.

Agricultural Emissions

Ammonia Emissions from Agriculture and Other Sources

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Abstract

Emissions of ammonia play an important role in the formation of fine particles in the atmosphere. Under typical atmospheric conditions, ammonia reacts with gaseous emissions of sulfur dioxide and oxides of nitrogen to form sulfate and nitrate fractions of fine particles (defined as particles less than 2.5 microns in aerodynamic diameter). In many parts of the United States, this fraction is as much as 50% of the total fine particle mass.

Thus, there is an urgent need for better quantification of ammonia emissions. There is also a need for high spatial and temporal resolution of ammonia emissions at scales that are compatible with input requirements for sophisticated chemical transport models. While inventories for many regulated species such as sulfur dioxide and nitrogen oxides are generally available with high resolution, such inventories for ammonia are much less common. Yet knowledge of ammonia emissions at high spatial and temporal resolution is necessary to reliably predict atmospheric concentrations of fine particles.

Many inventories in use today have been derived from the NAPAP inventory of 1985. The NAPAP numbers are often updated using economic factors to artificially “grow” the inventory rather than using real data, even when such data are readily available. This is partially because inventories can consist of thousands of spreadsheets, and it is a great deal of work to update all of these spreadsheets when new data become available. Thus, a key problem with existing ammonia inventories is that they are typically constructed for a specific year and location and do not have the capacity to be easily revised and updated. Nevertheless, there are several reasons why an inventory should be flexible enough to accommodate new information as it becomes available:

- An inventory is typically developed for a specific year. However, end users often need to modify the inventory to reflect a different year.
- Existing activity levels and emission factors for sources of ammonia are uncertain. When better values are released, it is important to include them in the inventory.
- It is sometimes difficult to perform sensitivity analyses using existing inventories. Such analyses are critical in quantifying the contribution of various sources; for example, when considering alternative control strategies.

To remedy this situation, a national ammonia emission inventory has been created in a format that will easily accommodate new information. Instead of a static file, the inventory is in the form of a model that is designed to allow the user to easily update emission factor or activity level data and then regenerate the desired output. Although there are currently many research groups working to improve emission factor and activity level data, some of these data are still of poor quality. Once new data are available, it will be easy to replace the outdated factors in the inventory. This structure also makes it possible to perform sensitivity analyses, an important tool for both regulators and modelers. Furthermore, the output is compatible with ARCVIEW, a GIS program. This is important both because the user is then able to view the inventory graphically, and because ARCVIEW files are compatible with EMS95, a common preprocessor to many atmospheric chemistry models. Thus one of the main contributions of this work is not simply a new national inventory but a framework that makes it possible to easily adjust and modify this inventory for use in different applications.

Measuring and Modeling Gaseous NH_3 and Aerosol NH_4 at the Regional Scale: How Does Ambient Concentration Respond to Emission Controls?

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Abstract

Controlling emissions of NH3 from agriculture is notoriously difficult, as it combines an inadequately known science covering a very disparate range of activities in a complex industry with social and political issues. Thus the modest reductions in many countries could be viewed as significant progress. With this background, it is helpful to show from a combination of monitoring and modeling approaches, the responses of both ambient concentrations and the gas to aerosol partitioning to changes in emissions. In this paper, changes in the chemistry of the atmosphere over the United Kingdom and other countries in Europe during a period in which emissions of SO2, NOx and NH3 have changed appreciably are explored from monitoring data and using a long range transport models. Sulphur emissions in the UK declined by 80% between 1986 and 2005, from 2300 kT S annually in 1986 to 400 kT S in 2005. During the same period emissions of NH3 declined by just 15% to 300kT. NH3-N and emissions of NOx declined by about 45%, to 450 kT NOx-N. The effect of these emission reductions changed the acidic aerosol mixture in the 1980s dominated by (NH4)2SO4 and NH4HSO4 to a more neutral aerosol dominated by NH4NO3 in recent years. Concentrations of HNO3 also increased during this period and the very different fractionation of both oxidized and reduced nitrogen species with different atmospheric lifetimes leads to substantially different deposition footprints for each of the pollutants and different patterns of deposition relative to those of the 1980s. To secure the greatest reduction in deposition in the near field for NH3 (<10km), it is necessary to reduce the emission directly. At the larger (regional) scale (10km to 200km) changes in atmospheric composition have increased the transport distance of NH3 and in principle partitioned more of the deposition as dry deposition. Long term monitoring data show a small decline in wet deposition of NH4+, consistent with the changes in chemistry, but overall, the response are small.

Odor Emissions and Chemical Analysis of Odorous Compounds from Animal Buildings

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Abstract

Odor emission from animal production buildings is a critical local issue according to the National Research Council report to the livestock and poultry industries (NRC, 2003) and people living and working near these operations. Even though federal and some state agencies do not regulate odors, emission of odorous compounds remains a high priority for animal producers (for siting new and expanding existing operations) and for neighbors living near livestock and poultry operations. There is an urgent need for odor emission factors from animal confinement buildings since very limited data is presently available. Odor emission factors are needed as inputs into dispersion models so odor concentrations can be calculated for existing and future livestock and poultry operations and utilized for the addition of control technologies on current operations and the siting and design of new facilities. This study will supplement the National Air Emissions Monitoring Study (NAEMS), which will soon be announced, with comprehensive measurements of odor emissions from eight separate animal buildings in the U.S. The NAEMS will monitor air emissions at swine and layer sites, and potentially at turkey, broiler, and dairy production facilities. The NAEMS will help livestock and poultry producers to comply with EPA regulations concerning regulated gases and particulate matter by monitoring these pollutants continuously for 24 months to fulfill the requirements of a consent agreement. Although odor is the air pollutant that plagues the animal industry with the greatest overall challenge, it is not included in the NAEMS because the EPA does not regulate it. One of the specific goals of the NAEMS is to provide the basic infrastructure for add-on projects that conduct additional measurements. Investigators in this project will add odor emission measurements to the NAEMS. The measurements will include both standard human sensory measurements using dynamic forced-choice olfactometry and a novel chemical analysis technique for odorous compounds found in these emissions. The sensory and chemical methods will be correlated to gain both quantitative and qualitative understanding of odor emissions from animal buildings.

Introduction

Odor emission from animal production buildings is a critical local issue, according to the National Research Council report to the livestock and poultry industries (NRC, 2003) and people living and working near these operations. Even though federal and some state agencies do not regulate odors, emission of odorous compounds remains a high priority for animal producers (for siting new and expanding existing operations) and for neighbors living near livestock and poultry operations. There is an urgent need for odor emission factors from animal confinement buildings since very limited data is presently available.

This study proposes to supplement the air emissions monitoring 2006-2009 National Air Emissions Monitoring Study (NAEMS) with comprehensive measurements of odor emissions. The NAEMS will monitor barn emissions at swine, dairy, broiler and egg layer facilities. The NAEMS will help livestock and poultry producers to comply with the Environmental Protection Agency (EPA) regulations concerning regulated gases and particulate matter by monitoring these pollutants continuously for 24 months to fulfill the requirements of a consent agreement. Although odor is the air pollutant that plagues the animal industry, it is not included in the NAEMS because it is not regulated by the EPA.

The odor measurements to be made in this study includes both standard human sensory measurements using dynamic forced-choice olfactometry and a novel chemical analysis technique for odorous compounds found in these emissions. The sensory and chemical methods would be correlated to gain both quantitative and qualitative understanding of odor emissions from animal buildings. The specific objectives of this study include: (1) determine odor emission factors of the NAEMS sites using common protocol and standardized olfactometry for use in air dispersion models and evaluation of controls, (2) develop a comprehensive chemical library that delineates the most significant odorants and correlate this library with olfactometry results for the NAEMS sites, and (3) disseminate information to stakeholders, including producers, agencies, regulators, researchers, local government officials, consultants, and neighbors of animal operations.

Background

Livestock and poultry producers in the United States are becoming increasingly concerned over the odors and gases that are generated and emitted from their animal operations. Odors and gas emissions from animal production sites are impacting producers in a variety of ways. Complaints from neighbors are increasing. Local units of government (counties and townships) have or are considering the establishment of setback requirements from rural residences and livestock operations to prevent odor and other nuisance complaints. State and federal regulatory agencies have begun to enforce existing air standards or enact new standards. These enforcements are being addressed during environmental review procedures of state or federal permitting processes.

Because of these growing concerns, there is a need to determine odor and gas emissions levels from animal production sites, such as the buildings, associated manure storage units, and on-farm outdoor feed storages. Emissions need to be known so producers and others can determine which sources are the major contributors. Individuals can then develop an air emission strategy for their operation. Unfortunately, quantifying air emissions from animal agriculture is a complex process. First, the complexity arises from the multitude and variety of individual sources responsible for emissions, the extreme variability of these emissions, and the variety of gaseous components being emitted. Secondly, robust method(s) are necessary to collect emission data from these sources, which involve the measurement of both the concentrations of the contaminant and the airflow rate from the source. Few researchers and engineers have taken on the task of measuring odor and/or gas emission rates because of these and other difficulties.

Most livestock and poultry odors are generated by the anaerobic decomposition of livestock wastes such as manure (feces and urine), spilled feed, bedding materials, and wash water. This decomposition of organic compounds results in the production of odorous volatile compounds that are metabolic intermediates or end products of microbial processes (Zhu et al., 1999). Many of these compounds are then carried by airborne particulates (NCARS, 1995) and dispersed into the atmosphere.

Most odors are a mixture of many different gases at extremely low concentrations. The composition and concentrations of the gas mixtures affects the perceived odor. To completely measure an odor, each gas would need to be measured. Most odorous gases can be detected (smelled) by humans at very low concentrations (Table 1). The fact that most odors are made up of many different gases at extremely low concentrations makes it very difficult and expensive to determine the exact composition of an odor.

Odor Measurements

There are two general approaches used to measure odor, either measure the concentrations of each important odorant gas or use olfactometry to evaluate the entire mixture using the human nose. Both approaches have strengths and weaknesses. Future developments will hopefully close the gap between the two approaches.

The specific individual gaseous compounds in an air sample can be identified and measured using a variety of sensors and techniques. The results can be used to compare different air samples. With good sensors and proper techniques, valuable information about the gases that emanate from a source can be collected and evaluated. Gas emission rates and control techniques can be compared rigorously. Regulations can be established to limit individual gas concentrations.

However, the gas measurement approach has some weaknesses when used to measure and control odors. The greatest weakness of the gas measurement approach is that the relationship between specific gas concentrations in a mixture and their perceived odor are unknown (Ostojic and O'Brien, 1996). As a result, regulations based on gas concentrations may reduce specific gas emissions and concentrations but not adequately address the odors sensed downwind by the neighbors.

Table 1. Odor threshold for selected chemicals found in livestock odors (Kreis, 1978)

Chemical	Odor Detection (ppm)
Aldehydes	
Acetaldehyde	0.21
Propionaldehyde	0.0095
Volatile Fatty Acids	
Acetic acid	1.0
Propionic acid	20.0
Butyric acid	0.001
Nitrogen containing	
Methylamine	0.021
Dimethylamine	0.047
Trimethylamine	0.00021
Skatole	0.019
Ammonia	46.8*
Sulfur containing	
Methanethiol	0.0021
Ethanethiol	0.001
Propanethiol	0.00074
t-Butythiol	0.00009
Dimethyl sulfide	0.001
Hydrogen sulfide	0.0072

*More recent values are 1 to 5 ppm (Reynolds, et al. 1998)

People have proposed using "indicator" gases to quantify livestock odors. Hydrogen sulfide and ammonia are among the most common chemicals proposed. Unfortunately, hydrogen sulfide and ammonia concentrations are not well correlated to livestock odor (Spoelstra, 1980; Pain and Misselbrook, 1990; Jacobson et al., 1997; Zahn et al., 1997). Yashuhara (1980) found that a mixture of 11 compounds strongly resembled the quality and character of solid swine manure. Livestock odors consist of many gases at extremely low concentrations, which are very difficult and expensive to measure. Measuring some of the gases may not be enough to describe the odor. Research and development of new, better, and lower cost sensors is ongoing. Electronic noses, which use electronic sensors to measure a select number of chemical compounds, are being used in some industries for quality control of various odor-producing processes. Most studies indicate that the outputs of electronic noses do not correlate with livestock odors (Watts, 1992; McFarland and Sweeten, 1994); however, one study suggests that technological developments may make it possible in the future (Misselbrook et al., 1997).

Malodor characterization is among the most demanding of all analytical challenges. This occurs because it is usually the case that aroma or odor critical components are present at very trace levels in a complex matrix of odor-insignificant volatiles (Wright et al, 1986). A large body of excellent analytical work has been reported during the past three decades relative to the volatile compounds emitted by high-density livestock operations. Scores of volatile compounds have been identified in these environments utilizing various concentrating and analytical techniques (Mosier et al. 1973; Hutchison et al. 1982; Oehrl et al. 2001; Keener et al. 2002; McGinn et al. 2003; Nielsen et al. 2004). Included among these volatiles are a large number of compounds that are known to be potent individual odorants (Devos et al. 1990). The challenge relative to the odor issue is to extract from this large field of "potential" odorants, the compounds that constitute the primary odor impact relative to these environments. Given sufficiently comprehensive and accurate reference and analytical data regarding the volatile compounds present in these environments, it would seem possible to accurately predict and rank the primary odor impact compounds. However, from a practical standpoint, this does not produce satisfactory results in most cases. The factors working against such success are incomplete or imprecise odor threshold data in concert with the extremely low odor thresholds of many if not most of the key odorants present.

A practical alternative is to carry out GC-olfactometry (i.e. GC-O)-based odor profile ranking studies relative to in-situ headspace volatiles collections taken directly from the target environment. This is the approach that is routinely taken in investigating odor issues surrounding matrices for which limited volatiles compositional data are available. The general experimental approach is to develop a detailed odorant ranking profile for a sensory graded "worst" case sample. Performing equivalent comparative odorant ranking profile analysis for equivalent sensory graded "best" case samples will typically indicate which of the "potential" odorant(s) present in the field account for the odor character differences between the two samples.

The necessity of prioritizing the individual odor carrying volatiles relative to a particular malodor issue is often overlooked in odor-focused investigations. Over the past decades, such prioritization is essential to the resolution of the typical crisis-driven malodor problems. Scores of these investigations have been successfully affected during this period; ranging from aroma and flavor complaints in foods and beverages to malodors in packaging, consumer products, and work environments. Collaborative efforts undertaken with Texas A&M - Texas Agricultural Experimental Station, Amarillo (Koziel) and West Texas A&M, Canyon (Parker) are directed at applying to high-density livestock operations some of the lessons learned in addressing these past, highly-diverse odor-focused investigations (Wright et al., 2004). Odor profiling by GC-O has proven to be an essential element required for defining, prioritizing. and tracking the basic building blocks of odor character in complex matrices (Wright et al., 1986; Nielsen et al. 2001; Willers et al. 2003).

Figure 1 is an "aromagram" that was generated by the GC-O investigator (shown in use in Figure 2) monitoring the odor impact of the individual compounds as they elute from the GC column. The retention time span of the peaks reflects the start and end time for the individual odor responses while the peak height reflects the perceived intensity of these responses. By overlaying these sensory responses with the MS signal, it is possible to correlate the sensory responses with corresponding electronic signals and odorant identification, respectively. At least 66 discrete odor notes were detected under the conditions of collection and many of these reflected intense to overwhelming odor intensities. The full range of previously reported swine farm odorants were detected, including: H_2S and its organic homologs; trimethylamine; VFA's, ranging from acetic to octanoic; phenolics, including phenol, p-cresol and p-ethyl phenol; indole, skatole and a wide variety of ketones, diones, and aldehydes, among others. A summary of a few of the major odorant compounds from this odor profile analysis is presented in Table 2.

Olfactometry, the most common sensory method, uses trained individuals and standardized procedures to measure odor levels and describe odors (see figure 3). The key advantage of olfactometry is the direct correlation with odor and its use of the human's highly sensitive sense of smell. Olfactometry also has the advantage that it analyzes the complete gas mixture so that contribution of each compound in the sample is included in the analysis. There are different olfactometry techniques. Data collected by different techniques can be neither combined nor directly compared.

McFarland (1995) reviewed many of the current olfactometry techniques being used for odor measurement and concluded that dynamic forced-choice olfactometry appears to be the most accepted method. Olfactometry suffers from a lack of precision compared to some of the sophisticated chemical sensors available. The lack of precision in olfactometry is due in part to the variability in each person's sense of smell and their reaction to an odor. Also, olfactometry does not identify the individual compounds that make up the odor. Even though olfactometry has limitations, it still is the best technique available for directly measuring odors at this time.

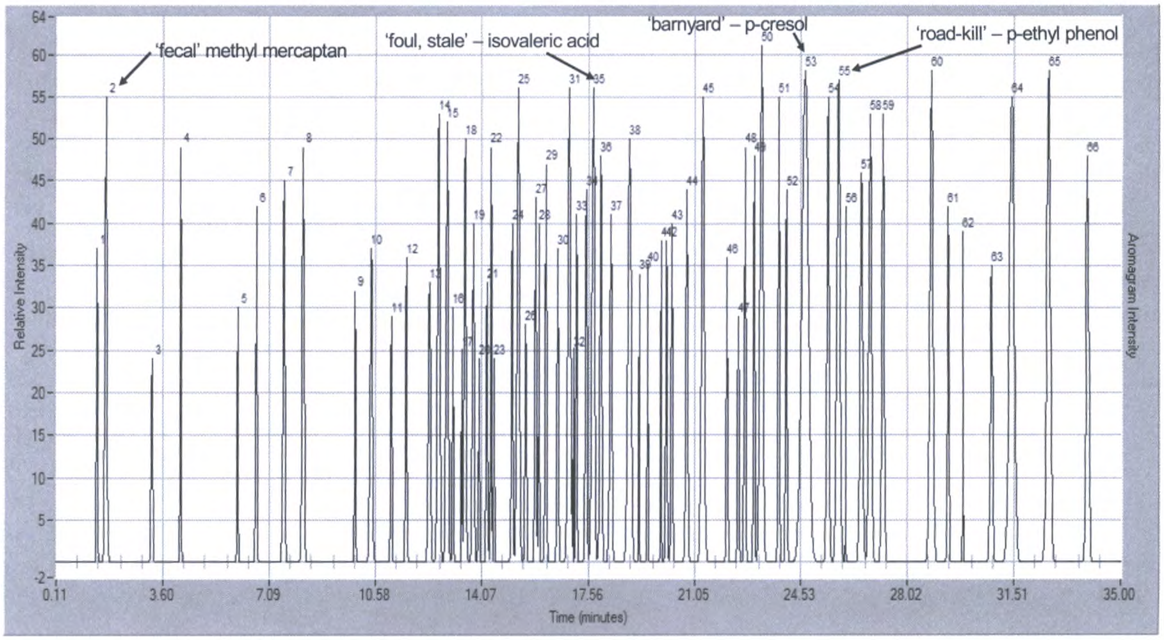

Figure 1. Aromagram from SPME odor collection at the exhaust fan of a swine finish barn.

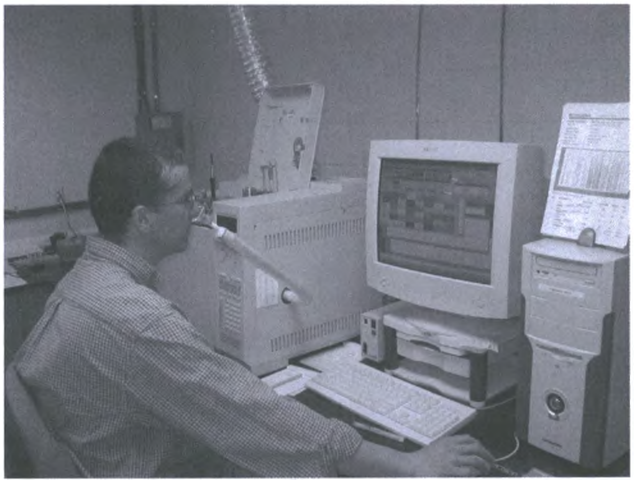

Figure 2. Real-life photo of Aroma Trax™ MDGC-olfactometry system.

Table 2. Representative odorants from inside a tunnel-ventilated swine finish barn collected with SPME near the exhaust fan.

Peak Number	GC Column Retention Time (min)	Odor Descriptor	Preliminary Odorant Identification
1	1.42	foul, fecal	hydrogen sulfide
2	1.68	fecal	methyl mercaptan
3	1.70	fishy	trimethylamine
4	4.15	buttery	diacetyl
6	6.60	amine	unknown amine or diamine
7	7.60	grassy	hexanal
10	10.30	buttery	pentanedione
14	12.60	savory, nutty	dimethyl pyrazine
18	13.45	musty, vinegar	acetic acid
20	13.85	fecal	dimethyl trisulfide
25	15.20	vomitus, body odor	propionic acid
27	15.85	cardboard, musty	? nonenal
31	16.80	vomitus, body odor	butyric acid
35	17.60	body odor, foul	isovaleric acid
38	18.80	foul, characteristic	valeric acid
45	21.30	medicinal	guiacol
50	23.14	medicinal, floral	phenol
52	24.10	beet, vegetable	geosmin
53	24.40	barnyard, characteristic	para-cresol
54	25.80	roadkill, decay, foul	para-ethyl phenol
58	27.15	taco shell, bat cave	2'-aminoacetophenone
60	28.70	outhouse	para-vinyl phenol
62	29.83	outhouse	indole
63	30.70	outhouse, naphthalenic	skatole
64	31.26	floral, honey	phenyl acetic acid
65	32.50	taco shell, bat cave	1-(2-aminophenyl)-1-butanone

Figure 3. AC'SCENT® International Olfactometer in use by sniffer and panel leader.

Odor must first be quantified to determine odor emission values. The most common and frequently reported measure of odor is dilutions-to-threshold. Diluting air samples with a known amount of odor-free air and presenting the dilutions to a panel of people using an olfactometer, which is an air dilution device, determines this value. Dilutions-to-threshold is the volume of odor-free air required to dilute a unit volume of odorous sample air to the point where it can be detected by 50% of a trained group of panel members (Nòren, 1987). Odor units are defined by CEN (2001) as the mass of odorants in one cubic meter of air at the odor detection threshold (1 D/T). The odor concentration of a sample is therefore expressed as odor units per cubic meter (OU/m^3) for calculation conveyance of odor emission rates (CEN, 2001). Odor emission rates (OU/s) from a livestock building or manure storage unit are the product of the ventilation airflow rate (m^3/s) through the barn or over the storage and the odor concentration (OU/m^3) in the exhaust air (Lim et al., 2001). To allow comparison with other research results, odor and gas emission rates are often specified to the number and weight of animals by dividing the total emission rate by the number of animal units (AU), where one AU is equal to 500 kg of animal live weight (Ni et al., 2000a; Wathes et al., 1997). Area-specific emission rates are determined by dividing the total emission rate by the emitting surface area (Gay et al., 2002; Groot Koerkamp et al., 1998).

Few researchers have attempted to quantify odor and gas emission rates from animal housing, and results are widely variable. Table 3 lists odor emission rates measured from buildings for various animal species. This variation likely stems from the lack of standardized methods used to measure both odor concentration and emissions. Lim et al. (2001) evaluated odor emission and characteristics at two commercial swine nurseries during the spring. Five sampling visits were made to each nursery and nine or 10 air samples were collected during each visit. Zhu et al. (2000b) measured odor at seven different facilities to determine daily variations. Air samples were collected every two hours over a 12-hour period during the day. Watts et al. (1994) measured odor emissions from a feedlot pen using a portable wind tunnel over a 5-day period following 64 mm of rain. The highest emission occurred about 48 hours after the last rainfall. The peak odor concentration was about 60 times higher than odors from the dry pen.

Table 3. Odor emission rates from animal housing

Species	**Production unit**	**Location**	Odor Emission Rate **OU m^{-2} s^{-1}**	**Reference**
Pigs	Nursery (deep pit)	Indiana	1.1-2.7	Lim et al. (2001)
	Nursery	Minnesota	7.3-47.7	Zhu et al. (2000b)
	Finishing	Minnesota	3.4-11.9	Zhu et al. (2000b)
	Farrowing	Minnesota	3.2-7.9	Zhu et al. (2000b)
	Gestation	Minnesota	4.8-21.3	Zhu et al. (2000b)
	All types	Minnesota	0.25-12.6	Gay et al. (2002)
Poultry	Broiler	Minnesota	0.1-0.3	Zhu et al. (2000b)
	All types	Minnesota	0.3-3.5	Gay et al. (2002)
Dairy	Free-stall	Minnesota	0.3-1.8	Zhu et al. (2000b)
	All types	Minnesota	1.3-3.0	Gay et al. (2002)
Beef	Feedlot	Minnesota	4.4-16.5	Gay et al. (2002)
	Feedlot	Australia	12.5-725	Watts et al. (1994)

Gay et al. (2002) have recently summarized odor emission rates from over 80 farms in Minnesota. Mean values for swine housing varied from 0.25 to 12.6 OU m^{-2}s^{-1}, poultry housing from 0.32 to 3.54 OU m^{-2}s^{-1}, dairy housing from 1.3 to 3.0 OU m^{-2}s^{-1}, and beef feedlots from 4.4 to 16.5 OU m^{-2}s^{-1}. Ventilation rates for mechanically ventilated buildings were calculated as the sum of the airflow rates for each fan. Fan airflow rates were determined by measuring static pressure across the fan using a manometer and referring to fan rating tables for the corresponding airflow values. For naturally ventilated barns, rates were estimated using mass exchange rates based on the carbon dioxide (CO_2) level between the inside and outside of the buildings. Although there is reasonably high variability, this data set suggests that odor emissions from swine housing and beef feedlots are higher than emissions from poultry and dairy housing.

The USDA-IFAFS funded a six-state project entitled “Aerial Pollutant Emissions from Animal Confinement Buildings” or APECAB, which is nearing completion and has quantified and characterized baseline emissions of odor, NH_3, H_2S, PM_{10}, and TSP from four types of swine buildings and two types of poultry buildings. The APECAB study (Jacobson and Heber, PIs) is a collaboration of land-grant universities in Minnesota, Indiana, Iowa (Hoff, Co-PI), Illinois, North Carolina, and Texas (Koziel, co-PI, Parker collaborator). The study is utilizing common instrumentation and protocol. At each measurement site, a mobile instrument trailer is stationed between two identical or nearly identical mechanically-ventilated, confined animal production buildings, and emission measurements are quasi-continuous. An instrument trailer houses a gas sampling system (GSS), gas analyzers, environmental instrumentation, a computer, data acquisition system, controller units for the real-time PM monitors, calibration gas cylinders, and supplies and equipment needed for the study. Gas concentrations are measured at the air inlets and outlets of each building while simultaneously monitoring total building airflow rates. Odor samples were taken biweekly to determine odor emissions. Emission rates are calculated by multiplying concentration differences between inlet and outlet air by building airflow rates. The 15-month sampling duration for the APECAB project assures that long-term emissions and annual emission factors can be fully characterized. Long-term measurements allow the recording of variations in emissions due to seasonal effects, animal growth cycles, and diurnal variations.

As mentioned above, odor measurements during the APECAB study were made every two weeks at the sampling site. Air samples are taken at the exhaust and inlet locations in each of the two barns from each site and analyzed by similar olfactometry laboratories at each cooperating university. An example of the preliminary findings for the odor emission data from two gestation barns in Minnesota is shown in Figure 4.

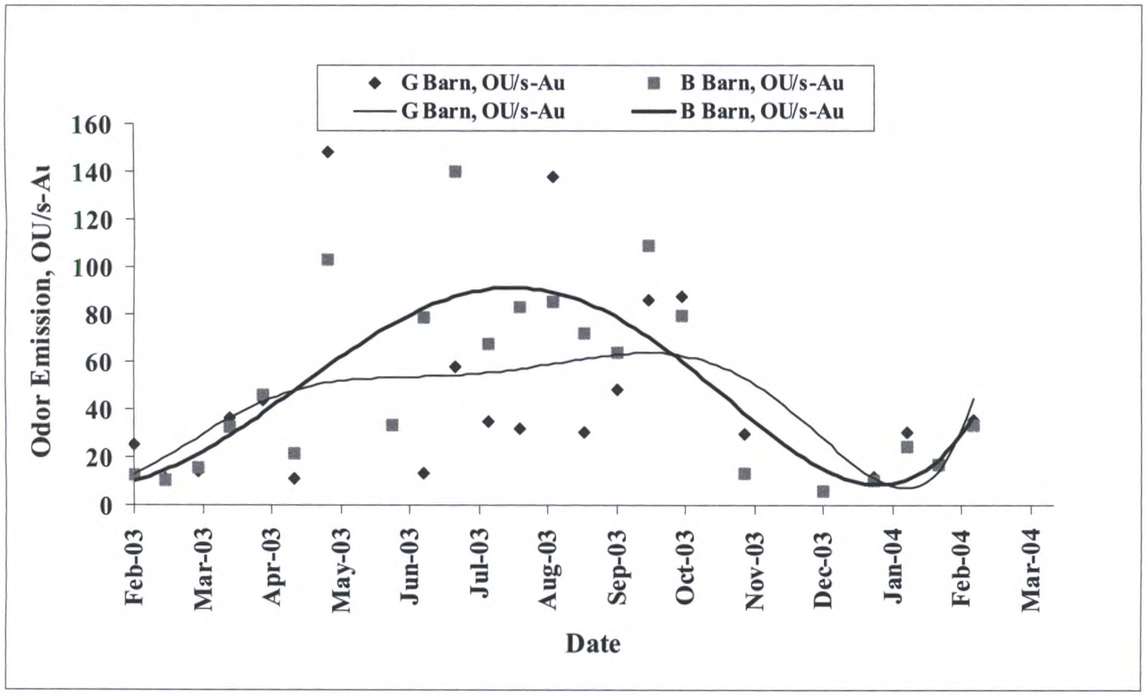

Figure 4. Odor emissions for two Minnesota sow gestation barns from Oct. 8, 2002 to Mar. 4, 2003.

Conclusions

This project will start collecting data later this year (2006) when the EPA's National Air Emissions Monitoring Study (NAEMS) begins. Selection of sites will be made during the spring/summer of 2006 and will include swine, poultry, and dairy sites. Measurements during the study will include both standard human sensory measurements using dynamic forced-choice olfactometry and a novel chemical analysis technique for odorous compounds found in these emissions.

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Effects of Reduced Crude Protein on Gaseous Emissions and Swine Performance

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Abstract

The effect of feeding reduced crude protein (CP) diets on air emissions was evaluated using groups of barrows housed in rooms with continuously measured gas concentrations and airflows. Pig weights and feed intake were recorded weekly over the course of four feeding phases: G1 (beginning at 24.5 kg body weight, BW), G2 (55.3 kg BW), F1 (87.2 kg BW), and F2 (111.4 kg BW). Pigs were offered one of three pelleted isocaloric, isolysinic diets: a control diet (C), a low crude protein diet (LCP) and an ultra low crude protein diet (ULCP), each supplemented with varying amounts of amino acids. Formulated CP of G1 was 22.5, 20.0, and 18.4% for the C, LCP, and ULCP diets. As feeding phases progressed there was a decrease in the formulated CP such that F2 was formulated to contain 16.6, 15.4, and 13.8% CP in the C, LCP and ULCP diet. Dietary treatment had no significant effect on animal performance ($P<0.05$). Pigs fed the LCP diet had greater intakes than pigs fed the C or ULCP diets during the grower phases but reduced intake during both finisher phases ($P=0.0287$). A diet effect was observed for average daily ammonia concentrations ($P<0.0001$). Exhaust ammonia (NH_3) concentration in rooms where pigs were fed the LCP diet were 16% less than the C diet (3.86 vs. 4.57 ppm). Ammonia concentrations were reduced 25% (2.93 ppm) in the ULCP diets compared to the LCP diet and 36% compared to the C. Airflow-corrected daily average NH_3 emission rates were 26.8, 21.0, and 14.5 mg min^{-1} for the C, LCP, and ULCP diets, respectively, corresponding to a daily mass of NH_3 emitted per kg of animal live weight, of 88.0, 68.9, and 46.0 mg kg^{-1}. Feeding phase effects were observed for NH_3 concentration, NH_3 emission rate, daily mass emitted and daily mass per unit of live weight with increases from G1 to G2 followed by a decrease from F1 to F2. Similarly, feeding phase effects were observed for hydrogen sulfide concentration and daily emitted mass of hydrogen sulfide per unit of live weight. Hydrogen sulfide concentration and emissions were not different between rooms offered the different dietary treatments ($P>0.05$). Diet had no effect on wet or dry mass of manure produced however TKN and NH_3-N concentration decreased with decreasing diet CP (7.9, 6.7, 5.7% and 5.4, 4.4, and 3.5%, respectively for C, LCP and ULCP diets).

Introduction

A new facility was constructed at Iowa State University specifically for the purpose of evaluating dietary effects on gaseous emissions. The facility became operational in September 2004, and a swine study was begun that same month. The objective of this paper is to describe the facility's capabilities and present the findings of the first study. The study evaluated pigs that were fed either a typical industry diet or one of two diets that contained decreasing crude protein levels by supplementing with amino acids. Animal performance and gaseous emissions were measured.

Material and Methods

Forty-eight crossbred barrows (initial bodyweight = 18 kg) were allocated to one of eight environmental rooms (six pigs per room). A 2-wk acclimation period occurred prior to the start of the feeding trial. Pigs were offered one of three pelleted isocaloric, isolysinic diets: a control diet (C), a low crude protein diet (LCP) and an ultra low crude protein diet (ULCP), each supplemented with varying amounts of amino acids. The C and the LCP diets were offered in three, each, of the eight rooms and the ULCP diet was offered in the remaining two rooms. Formulated CP of G1 was 22.5, 20.0, and 18.4% for the C, LCP, and ULCP diets. As feeding phases progressed there was a decrease in the formulated CP such that F2 was formulated to contain 16.6, 15.4, and 13.8% CP in the C, LCP and ULCP diet. Pig weights and feed intake were recorded weekly over the course of four feeding phases: G1 (beginning at 24.5 kg BW), G2 (55.3 kg BW), F1 (87.2 kg BW), and F2 (111.4 kg BW). At the start of each feeding phase, diet assignments were randomly assigned to the eight rooms. Pigs were allowed ad libitum access to feed and water. A light schedule was programmed to provide light in each room from 0700 h to 1800 h daily. During each feeding phase, excreted manure was sub-sampled and weighed in order to provide estimates of volume and nutrient content excreted from each treatment.

Exhaust air from each room was sampled in a consecutive manner; 15 min of sampling from a room followed by 15 min of sampling in the next room, and so on. Background measures of the incoming (outdoor) air was sampled in between each full round of room sampling. This provided a total of 10-11 daily observations in each room. All sampling was automated. Analyzers employed for sample analyses included a TEI Model 17C ammonia/NO_x chemiluminescence analyzer and a TEI Model 45C H_2S/SO_x pulsed fluorescence analyzer (Thermo Electron Corp., Franklin, MA). Airflow through each room was measured every 30 sec using differential pressure transducers calibrated for the pressure difference across orifice plates.

Results

Dietary treatment had no significant effect on ADG, ADFI or F:G ($P<0.05$). Pigs fed the LCP diet had greater intakes than pigs fed the C or ULCP diets during the grower phases but reduced intake during both finisher phases ($P=0.0287$).

A diet effect was observed for average daily ammonia concentrations ($P<0.0001$). Exhaust ammonia (NH_3) concentration where pigs were fed the LCP diet were 16% less than the C diet (3.86 vs. 4.57 ppm). Ammonia concentrations were reduced 25% (2.93 ppm) in the ULCP diets compared to the LCP diet and 36% compared to the C. Airflow-corrected daily average NH_3 emission rates were 26.8, 21.0, and 14.5 mg min^{-1} for the C, LCP, and ULCP diets, respectively, corresponding to a daily mass of NH_3 emitted per kg of animal liveweight, of 88.0, 68.9, and 46.0 mg kg^{-1}. Feeding phase effects were observed for NH_3 concentration, NH_3 emission rate, daily mass emitted and daily mass per unit of liveweight with increases from G1 to G2 followed by a decrease from F1 to F2. Feeding phase effects were observed for ammonia concentration, ammonia emission rate and the calculated variables (daily mass emitted and daily mass per unit of liveweight). Concentration and emission of ammonia generally increased through the grower phases then decreased during the finisher phases.

Similarly, feeding phase effects were observed for hydrogen sulfide concentration and daily emitted mass of hydrogen sulfide per unit of liveweight. Hydrogen sulfide concentration and emissions were not different as a result of dietary treatments ($P>0.05$). Though not statistically significant, this was unexpected because a sulfur-containing amino acid (methionine) was included in the LCP and ULCP diet, resulting in what was expected to be a reduced total dietary sulfur content. Diet analyses support no differences in total dietary sulfur content, leaving no apparent explanation for the observation, though non-significant. Feeding phase effects were observed for hydrogen sulfide concentration and daily emitted mass of hydrogen sulfide per unit of liveweight (calculated from concentration, airflow, and bodyweight measures), following the same trend as observed for ammonia, whereby there were increases from G1 to G2 followed by a decrease from F1 to F2. The interaction of diet and feeding phase was not significant for any variable tested.

Diet had no effect on wet or dry mass of manure produced, however; TKN and NH_3-N concentration decreased with decreasing diet CP (7.9, 6.7, 5.7% and 5.4, 4.4, and 3.5%, respectively for C, LCP and ULCP diets).

Discussion

Average daily ammonia concentrations reported in this study from swine fed the C diets are within the range of those reported by Zhu et al. (2000) who measured ammonia concentrations at the exhaust fan. Values reported here fall within the low end of values reported in a review by Arogo et al. (2003). Average daily hydrogen sulfide concentrations reported in this study are approximately 100-fold less than those reported by Zhu et al. (2000), who measured hydrogen sulfide concentrations at the exhaust fan.

Conclusion

The findings from this study demonstrate that reduced crude protein diets can be fed throughout the grow-finish phase with no detrimental effects on animal performance. The result from feeding such diets is substantial reduction in ammonia emissions. The facility demonstrated that it has the sensitivity to detect and quantify such differences, rendering this a feasible approach to establishing diet modification effects on mass of emissions from the farm.

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Detection and Enumeration of Airborne Microbial Pathogens Associated with Swine Farms in Eastern North Carolina

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Abstract

Animal agriculture has evolved so that large concentrations of animals are housed on relatively small parcels of commercial properties. These large concentrations of animals may have adverse impacts on environmental quality, including air quality, in close proximity to sites. Considerable work has focused on air quality associated with particulate, ammonia, and odor (odorant) emissions associated with farms. However, until recently, little research has addressed airborne microbial pathogens on farms. Of the current research, most has focused on air quality in the animal housing units. The focus of this research was to enumerate outdoor airborne pathogens and indicator microbes on farm properties, including at the upper and lower property boundaries. The objectives were to determine airborne microbial impacts both in close proximity to the waste management systems on the farms and at other locations, including at farm boundaries. Air samples were collected for microbial indicator and pathogens using standard all-glass impingers (AGI-30) and open-face filter cassettes for bacterial endotoxin analyses. Microbial concentrations of a suite of fecal and general indicator organisms, representative of bacterial, viral, and parasitic human pathogens, as well as the frank bacterial pathogen, *Salmonella*, were measured. The indicator organisms included: fecal coliform bacteria, *E. coli*, spores of *Cl. perfringens*, and coliphage as fecal indicators and total aerobic bacteria and total fungi as general air quality indicators. Bacterial endotoxins, generally associated with barn dust, also were measured throughout the farm properties. Microbial levels ranged from below detection limits to 1.7×10^6 cfu/m^3. Fecal indicator organisms were readily detected at most of the farm sites; however, *Salmonella* were not detected in air samples at any of the sites during the course of this study. Bacterial endotoxins, shown to have adverse health impacts to workers on the farms, were detected close to the barns, as well as at lower property boundaries at levels higher than those in upwind boundary samples for some of the study sites. Microbial concentrations were generally highest associated with barns that utilized tunnel ventilation, as compared to those that are naturally ventilated, and were generally higher at the lower property boundaries when compared to the upper property boundaries. These results suggest that there are airborne microbial impacts associated with swine farms in North Carolina and that these impacts may extend off of the property boundaries. These results have direct implications for future regulations concerning airborne microbial pathogens associated with confined animal feeding operations. The extent to which these increased airborne microbial levels pose actual human health risks is unknown and deserves further investigation.

Introduction

In the United States, confined animal feeding operations (CAFOs) have become the standard for large-scale animal production to supply the demands of a growing population. Because of the scale at which animals are produced, there are large quantities of fecal waste that are traditionally recycled for their nutrient value to crop agriculture not used for human consumption(Humenik, Rice et al. 2004). Typically, the system utilizes anaerobic treatment in lagoons followed by land application for manure that is handled as slurry, or direct land application following removal from the housing units for wastes that are traditionally handled dry. Because of the magnitude of fecal wastes produced by CAFOs, it is important to consider the environmental impacts that may be associated with these farming practices. These impacts may include fecal contamination of ground and surface waters in close proximity to the farm sites, airborne fecal contamination, and off-farm contamination associated with vectors, such as rodents and houseflies.

To date, there have been few environmental studies with the goal of determining airborne fecal contamination on agricultural sites outside of the housing units and at property boundaries. Several studies have focused on air quality inside the housing facilities, concluding that there is airborne microbial contamination within the barns that can lead to animal and human exposures(Cole, Hill et al. 1999; Bilic, Habrun et al. 2000; Chang, Chung et al. 2001; Allen, Hinton et al. 2003; Richardson, Mitchell et al. 2003). Another concern for airborne microbial exposures associated with CAFOs is antimicrobial resistance traits carried by bacteria, which may lead to the ineffectiveness of certain drugs for treating animal or human infectious diseases(2003; Gibbs, Green et al. 2004; Chapin, Rule et al. 2005). Finally, studies have shown that bacterial endotoxins, associated with dust from agricultural barns, can have adverse health effects for workers on farms, as well as for more susceptible populations living in close proximity to the farm properties(Clapp, Becker et al. 1994; Schwartz, Thorne et al. 1995; Thorne, Reynolds et al. 1997; Chrischilles, Ahrens et al. 2004; Kim, Ko et al. 2005; Merchant, Naleway et al. 2005).

Concerns about human and animal health risks from animal fecal wastes released by CAFOs have led to the development and evaluation of alternative manure treatment technologies for better management of animal wastes and to better control environmental impacts(Humenik, Rice et al. 2004). Airborne releases of microorganisms from CAFOs may be important pathways for pathogen movement off farms and has been poorly studied for conventional and advanced animal waste management technologies. The objective of these trials was to investigate and quantify the release of airborne microorganisms and endotoxins associated with swine CAFOs in North Carolina on the farm properties and at the property boundaries.

Methods and Materials

During the course of this study, air samples were collected at 17 different commercial swine farms throughout Eastern North Carolina. Waste management systems on the farms consisted of both conventional anaerobic lagoon-sprayfield systems as well as those that utilize advanced biological treatment and other alternative processes. For all of the sites, air samples were collected at the upper and lower farm boundaries, as well as at locations on the properties where airborne releases were expected, such as at the housing units, at locations where open air handling of fecal wastes occurred, and in areas on the farms where there was land application of treated waste residuals.

Two different types of air samples were collected to enumerate a suite of microbial indicator and pathogenic organisms. All-glass impingers (AGI-30) containing 1% peptone-water with 0.01% Tween 80 and 0.005% antifoam A were used in duplicate to collect air samples for the fecal indicator organisms: fecal coliform bacteria, *E. coli*, spores of *Cl. perfringens*, total coliphage, and the frank pathogen, *Salmonella*. Samples from the AGI-30s were also assayed for total aerobic bacteria and total fungi as general microbial indicators of air quality. The AGI-30s were operated for 30-minute intervals at a flow rate of 12.5 L/minute. In addition to the AGI-30s that were used to collect air samples for detection of airborne microbial and fecal indicator organisms, SKC personal samplers were used, with open-faced filter cassettes, to collect bacterial endotoxins at each of the sites on the farms where the AGI-30 were utilized(Thorne, Reynolds et al. 1997). These samplers were operated for 4-hour intervals at a flow rate of 4 L/minute (equivalent to roughly a cubic meter of air).

Total bacteria and fungi were analyzed using a spread-plate technique on R2A agar (bacteria) or MEA agar (fungi) respectively and were cultured aerobically at room temperature for 5 to 7 days. Fecal coliform and *E. coli* were enumerated using a most-probable number (MPN) format and a defined substrate medium (IDEXX Colilert, Portland, ME), with incubation at 37°C for 4 hours, followed by subsequent incubation at 44.5°C for 18 hours. *E. coli* from this system was further cultured on EC-MUG agar at 37°C overnight and then colonies were isolated for further characterization (BBL Enterotube II, Beckton Dickson, Sparks, MD) and antibiotic resistance testing by a micro-dilution assay system (TREK Diagnostic Systems, Cleveland, OH)(Sullivan 2004). *Cl. perfringens* spores were detected and quantified by an MPN assay using an iron milk medium method (IMM) with incubation for 24 hours at 41°C, following an initial heat treatment at 65°C for 20 minutes to inactivate the vegetative bacteria in the sample(St. John, Matches et al. 1982). Total coliphage were detected and quantified by two-step enrichment-spot plate lysis methods using *E.coli*

C3000 host bacteria (modified from EPA method 1601)(USEPA 2001). *Salmonella* was detected and quantified by an MPN method with pre-enrichment in buffered peptone water, enrichment in Rappaport-Vassiliadis broth, followed by streaking on *Salmonella-Shigella* agar for distinctive colonies. Colonies were isolated, biochemically confirmed, and subjected to antibiotic resistance testing using a micro-dilution method, as previously described(Vassiliadis 1983). Bacterial endotoxins were assayed by a *Limulus* Amebocyte Lysate assay in Peter Thorne's laboratory, University of Iowa(Thorne, Reynolds et al. 1997).

Environmental conditions were measured at the sites on farms where air samples were collected at the time of sample collection. The environmental parameters that were measured included: temperature, relative humidity, wind velocity, and solar irradiation (1.5 m height from the ground during the microbial air sampling).

Results

Results for mean bacteria and fungi concentrations are summarized in Figure 1. Bacteria concentrations ranged from 161 to 296,999 cfu/m^3. Fungi concentrations ranged from 118 to 5057 cfu/m^3. Farm 2 had the highest mean bacteria concentrations and Farm 16 had the lowest mean bacteria concentrations. Mean bacteria concentrations were more variable than mean fungi concentrations among the farm sites tested. Farm 3 had the highest mean fungi concentrations and Farm 10 had the lowest mean fungi concentrations.

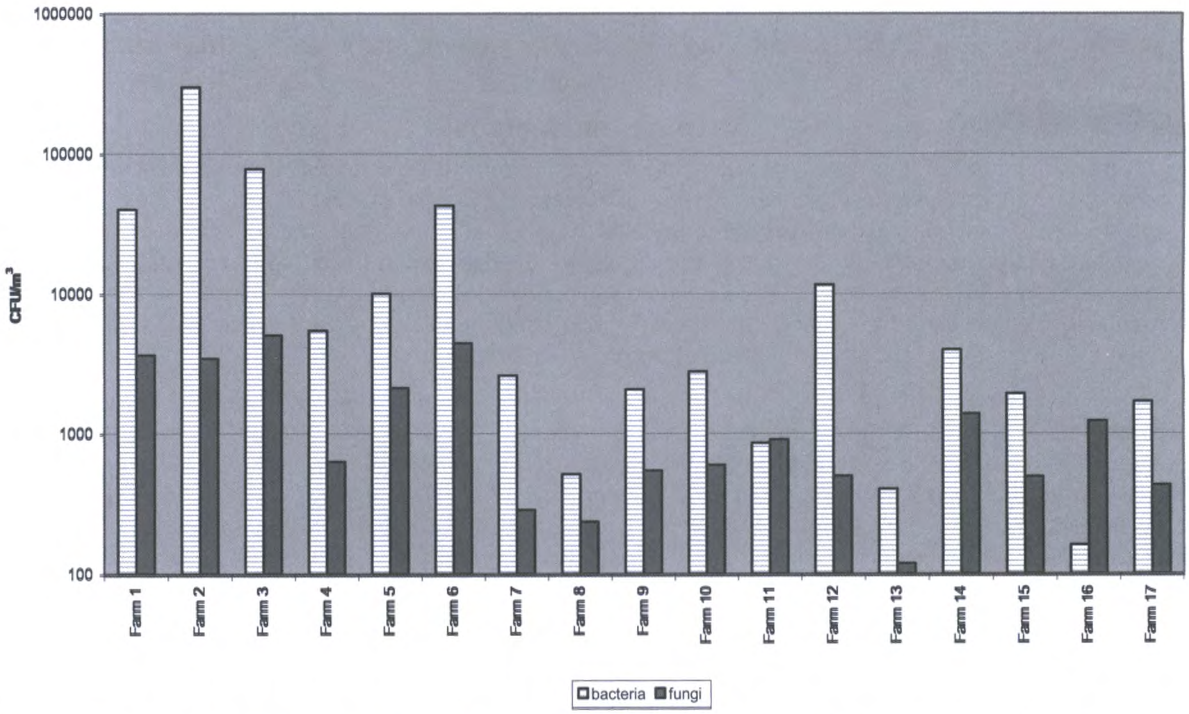

Figure 1. Mean Bacteria and Fungi Concentrations (CFU/m^3) in Air Collected on Farm Sites

Air samples were collected at multiple sites on each of the farms. The sites included, at minimum, the upper and lower boundary, and swine housing units (barns). Bacteria, fungi, and endotoxin concentrations for each of the sites at Farm 12 are shown in Figure 2. These results were typical of results for other farms in the study. Air samples were also collected during spray irrigation/land application events at farm sites when possible. Figure 2 shows bacteria, fungi, and endotoxin concentrations at the upper and lower boundary, at the barns, and upwind and downwind of the land application of treated liquid waste residuals.

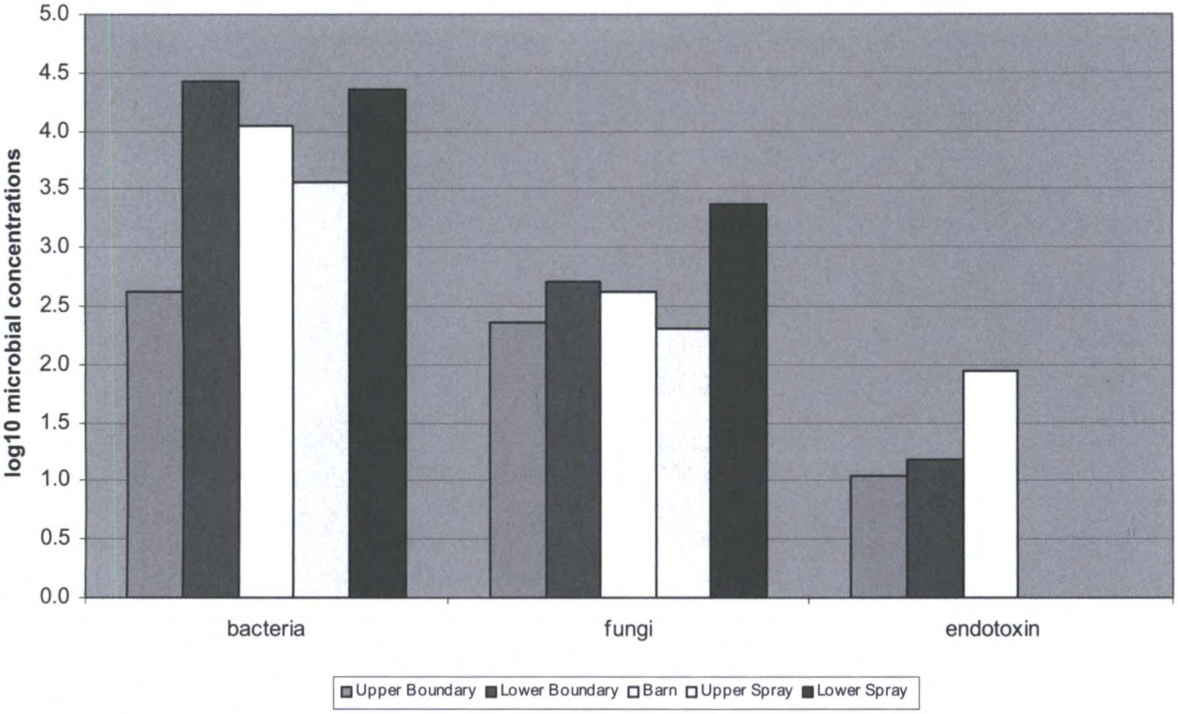

Figure 2. Bacteria, Fungi, and Endotoxin Concentrations at Various Locations on Farm 12

It is also important to take into account the concentrations of fecally associated microbes when measuring air quality on farm sites. Table 1 summarizes the number and percentage of samples that were positive for fecal microbes (fecal coliform bacteria, *E. coli*, spores of *Cl. perfringens*, and total coliphage) for each of the farms and the geometric mean and median concentrations where positive samples were detected. Fecal microbe occurrence ranged from below detection limits to an occurrence rate of 24% (at Farm 6). Geometric mean fecal microbe concentrations ranged from below detection limits to 154 cfu or pfu/m^3. Those farms with tunnel ventilation tended to have the higher percent positive rates and higher geometric mean and median concentrations of fecal microbes (data not shown).

Table 1. Percentage of Air Samples Positive and Geometric Mean and Median Concentrations of Samples Positive for Fecal Microbes

Location	Number Positive/Total Number (%)	Geom. Mean (Median) Concentration (cfu or pfu/cm3)
Farm 1	38/416 (9%)	154 (69)
Farm 2	37/193 (19%)	87 (100)
Farm 3	19/175 (11%)	90.7 (46)
Farm 4	1/85 (1%)	110 (110)
Farm 5	0/200 (0%)	-
Farm 6	29/120 (24%)	88 (70)
Farm 7	2/160 (1%)	32 (33)
Farm 8	3/112 (3%)	29 (32)
Farm 9	6/96 (6%)	96 (48)
Farm 10	6/80 (8%)	37 (36)
Farm 11	1/72 (1%)	10 (10)
Farm 12	10/152 (7%)	43 (53)
Farm 13	5/200 (3%)	43 (31)
Farm 14	5/120 (4%)	24 (31)
Farm 15	19/120 (16%)	63 (31)
Farm 16	0/24 (0%)	-
Farm 17	0/72 (0%)	-

Summary

As shown in Figures 1 and 2, all of the farms had measurable concentrations of total bacteria and fungi. In order to account for upwind, off-farm airborne contamination, upper boundary measurements were made at each of the farm sites. Figure 2 shows bacteria, fungi, and endotoxin concentrations typical of many of the farm sites tested. Microbial concentrations were generally lowest at the upper boundary, higher at the barns, and highest at the lower boundary. Additionally, for land application events, microbial concentrations were generally higher downwind of the practice as compared to the upwind sample. Endotoxin concentrations were generally low at the upper boundary, higher at the lower boundary, and highest near the barns. This is consistent with reports in the literature, as bacterial endotoxins are generally associated with dust from the barns. For each of the farms, it was noted which utilized tunnel ventilation, as opposed to being naturally ventilated (data not shown). Airborne microbial concentrations were generally highest associated with those farms that utilize tunnel ventilation for their housing units. In addition to the detectable levels of bacteria and fungi, there were also generally detectable levels of fecal microbes on these farm sites. The levels of fecal microbes ranged from below detection limits to a geometric mean concentration of 154 cfu or pfu/m^3. These results demonstrate that there is general and fecally associated airborne contamination associated with the sampled farms, as documented by the generally higher microbial concentrations at the lower property boundaries compared to the upper property boundaries. Bacterial endotoxins, associated with adverse health effects in humans, were detected throughout the properties at many of the farm sites. It is unclear the extent to which airborne microbial contamination extends off the farm sites and how this contamination might effect human health, however, these points deserve further study in the future.

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Modeling and Regulating Ammonia Emissions

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Introduction

In most European countries, animal husbandry is the major source of ammonia emissions. The source of ammonia emission within animal husbandry is the animal manure that is exposed in the following situations:

- Animal housing,
- Manure storage,
- Fields to which manure has been applied,
- Fields receiving excreta deposited by grazing animals.

The instantaneous emission from these sources is dependent on the characteristics of the manure (particularly the concentration of ammonium and pH) and the effectiveness of the mechanisms in the air that transport ammonia within the atmosphere. Since these latter processes are also responsible for the dispersion of ammonia in the atmosphere, the emission and dispersion processes are correlated. The processes driving ammonia emissions therefore change over time-scales that vary from the seasonal, reflecting some agricultural practices, to the daily or hourly, reflecting other agricultural practices and changes in atmospheric processes.

Within the framework of the UN Convention on Long-Range Transboundary Pollution (CLTRP), the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air pollutants in Europe (EMEP) is responsible for assessing the dispersion and deposition of nitrogenous compounds for Europe. The ammonia emissions used are generally reported by signatory countries as total annual emissions. The EMEP model imposes a temporal variation on the NH_3 emission totals derived from the results of GENEMIS project. This currently assumes that the seasonal variation is very similar across Europe, with a main maximum in early spring and a secondary maximum in October-November, despite the large variation in agricultural practices. Recognizing that this was a gross simplification of reality, a project was initiated under the auspices of the Nordic Council of Ministers to develop a model that would improve the temporal resolution of ammonia emission estimates. A second objective was the modeling of a range of ammonia abatement measures that either are or could be a part of the regulation of agricultural ammonia emissions.

The Model

The model is based on the principles previously described in Hutchings et al (1996) and Pinder et al (2004) when modeling ammonia emissions from dairy cattle farms. The two main principles are that the model should follow the fate of N excreted by livestock through the manure handling chain (housing, storage and field application) and should account for the major physical and chemical processes determining emission. The first principle enables simulation of the knock-on effect of changes in emission at the start of the chain on the emission from subsequent links. The second principle enables the model to describe the magnitude and temporal variation of emission from each source.

Ammonia is emitted whenever an aqueous solution of ammonium is exposed to an atmosphere in which the ammonia concentration is lower than in the air that is immediately above the surface of the solution. The formula underlying the instantaneous ammonia emission from the *i*th source (E_i) is:

$$E_i = \frac{A_i N_{A,i}}{H_i V_i r_i}$$

Where A_i is the area of manure exposed, $N_{A,i}$ is the amount of ammoniacal N present, H_i is a coefficient relating the concentration of ammonia at the surface of the solution to the concentration of ammonium, pH and temperature of the solution, V_i is the volume of manure and r_i is the resistance to ammonia transport from the manure to the free atmosphere. The sources of emission are animal housing (i=1), manure storage (i=2), field-applied manure (i=3) and manure deposited during grazing (i=4). The source of the ammoniacal N is the animal excretion and this flows through each of the emission sources, with progressive depletion by the gaseous losses. The area of the source is identified with the following; for animal housing, the floor and manure channels covered or containing excreta; for storage, the surface area of the store; for field-applied manure and manure deposited during grazing, the area of manure exposed. Calculation of the H_i coefficient requires knowledge of the temperature and pH of the manure. The temperatures are calculated for animal housing whereas air temperature is assumed for the other sources. The pH of manure in each source is assumed to be constant. The resistance to ammonia transport is calculated using a ventilation model for the animal housing and using standard micrometeorological principles for the other sources. The time steps used in the model are determined by the user but should normally be one hour or less.

The main changes relative to the previous models are the inclusion of modules to more realistically simulate animal housing with forced or free ventilation and the treatment of emissions from field-applied manure.

Animal house ventilation

The inside temperature and ventilation rate of animal housing with force ventilation are simulated using a simple energy model. This model assumes that the aim of management is to maintain the indoor temperature at a target value suitable for the animal species. The ventilation rate necessary to achieve this objective is calculated from the outside temperature and the sensible heat production of the animals. The sensible heat production is calculated from the total heat production, using the methods described in CIGR (2002). An empirical constant is then used to obtain the resistance to ammonia transport. The ventilation is assumed to be constrained between the lower and upper limits, for welfare and engineering reasons respectively. If the ventilation rate is constrained at the minimum level, it is assumed that supplementary heating is provided to maintain the indoor temperature at the target value. If ventilation is constrained at the maximum level, no mechanical cooling is assumed and the inside temperature is allowed to exceed the target level.

For freely ventilated housing, it is assumed as in Gyldenkærne *et al.* (2005) that farmers can partially control ventilation by opening or closing doors and air vents. At ambient air temperatures above freezing, this enables them to the inside temperature at a constant margin above ambient. The ventilation rate is then a constant that is estimated from. At ambient air temperatures below freezing, the model again follows Gyldenkærne *et al.* (2005) and assumes that the restriction of ventilation, combined with the ground heat flux and deposition of warm excreta, is sufficient to ensure that inside temperature never falls below freezing.

Field-applied manure

The fate of ammoniacal N in manure applied to the field is assumed to be determined by the competition between the processes of infiltration into the soil and volatilization into the atmosphere. The model treats the field-applied manure as if it were a leaky tank, in which the manure is maintained at a constant depth. Processes such as manure application or precipitation that increase the volume of field-applied manure increase the area of this tank whereas processes such as evaporation, infiltration or plowing that decrease the volume, decrease the area. Evaporation is made a function of solar radiation, temperature and wind speed, whilst infiltration is made dependent on the saturated conductivity of the soil and the dry matter content of the manure. To account for the effect of freezing on the infiltration rate, the infiltration rate was linearly reduced from 100% of the value determined by the soil and slurry properties at +1°C to zero at -1°C.

Simulations

The model was used to simulate an area with 30 000 finishing pigs (average weight 70 kg) with a daily excretion of 41g N, of which 70% is ammoniacal N. In the animal housing, the assumptions were a floor area of $1m^2$ per pig, fully slatted flooring, a volume of washing + spilt drinking water of 1.5 litre per pig per day, a target temperature of 20°C, a minimum temperature of 15°C, minimum and maximum ventilation rates of about 5 and 57 litres per pig per hour respectively and the handling of the manure as slurry. The surface area of manure storage was calculated on the basis of the number of months storage required and a depth of 4 m. For field application, a soil with an infiltration capacity of 72 mm d^{-1} was assumed and the application technique was assumed to be broadcast spreading. The application rate was 30 m^3ha^{-1} and manure was applied between the hours of 08.00 and 16.00, without incorporation by plowing. The maximum daily application rate was set to one fortieth of the maximum capacity of the manure storage. This is intended to reflect the variation in application date between farmers, rather than capacity limitations on any particular farm. The presence of well-developed arable crops was assumed to prevent field application of manure between mid spring and late summer. A synthetic climate was used, with daily mean air temperature and solar radiation varying sinusoidally over the year between -5 and +20°C, and 10 and 40 MJ d^{-1} respectively. Hourly air temperature was varied sinusoidally over the day, with a daily range of 10°C. A day length of 12 hours was used throughout, with solar radiation peaking at midday. The daily precipitation was 2 mm, evenly divided over the day. The wind speed was 2 ms^{-1} and neutral stability was assumed.

Three scenarios were investigated. In the first, no restriction was placed on the timing of the field application of manure, other than that due to the presence of a well-developed crop. This meant that the manure storage capacity could be limited to the equivalent of 3 months production. In the second, an additional restriction imposed by not making field applications during the winter. This is a common restriction in areas that are classified as nitrate sensitive under the EU Nitrates Directive. Manure storage capacity had then to be the equivalent to 6 months production. In the final scenario, a range of abatement methods were applied; the proportion of the floor area dirtied by animals was reduced by about 40%, a porous cover was placed on the manure storage and the field-applied manure was incorporated within 6 hours of application. Manure storage capacity was again equivalent to 6 months production.

The model has yet to be fully parameterised. The empirical constants used in modeling the housing and storage emissions were therefore adjusted to give annual emissions similar to the Danish standard values. The model was run for two years and the results from the second year are shown here.

Results

The results from the first scenario (Fig 1a) show a peak in animal house emissions in the summer, corresponding with the period of highest temperature and ventilation rate. The emissions from storage also peak in mid summer but are much lower. The emissions from field applications show a more complex pattern. During the late autumn, winter and early spring, the rate of application is limited by the rate of production of manure; there is little storage. There is a shallow peak in the mid winter that corresponds with the period when the soil is frozen and infiltration is reduced, giving a longer period during which the ammoniacal N in the manure can volatilize. Emissions fall in early spring as the frequency of sub-zero temperatures decrease but rise again, as the rise in temperature increases the volatilization rate. There is a peak in the early autumn, ending when the manure accumulated during the late spring and summer has been applied. Emissions during this autumn peak gradually fall as the temperature falls. The annual emissions are shown in Table 1.

In the second scenario (Fig 1b), the housing emissions are identical to the first scenario but the emissions from storage are higher, due to the larger surface area of the storage facility (Table 1). The restriction of manure application to the field to spring and autumn creates two large peaks of emission. Total field emissions are higher than in the first scenario because the concentration of manure application in the spring means that the temperature and radiation during the application period are higher. The higher storage and field emissions mean that the annual emission in the second scenario is higher than in the first. In the third scenario (Fig 1c), the pattern of emission is similar to the second scenario but all emissions are reduced, particularly those from the field applications.

Discussion

The scenarios used here demonstrate the large temporal variation in ammonia emissions from agriculture. This variation is caused partly by the weather but mainly by the farmers' responding to the weather, the cycle of crop production, the seasonal demand on labor and the regulatory environment. It is not yet clear how detailed a representation of these variations is necessary. Work by Sjoth *et al* (2004) suggests that a static estimate of farming activities, as can be obtained from a survey of management practices, may be adequate when comparing model results and measurements. However, if the objective is to predict past or future emissions, assess the likely impact of abatement measures or extrapolate research results to estimate emission factors, functional relationships relating farm management to more readily available data need to be developed.

In a lightly regulated environment, the short-term dynamics of farm management are likely to be driven predominately by the interplay of weather, livestock, crop and soil. At the EU scale, the Farm Structural Survey provides a good source of data on the geographic distribution of different farm types, the livestock species kept and the land holding. More detailed data may be available at the scale of the member state, but the varied nature and format of these data make them difficult to use. Soil type and land use data, including detailed cropping data are also available at the EU scale. Unfortunately, data that would enable livestock species to be distributed between combinations of type of animal housing, manure storage and field application method are either not collected or are not readily accessible.

Farming regulation can affect the management of manure both directly and indirectly. An example of an indirect effect is if farmers change their crop rotation, and therefore manure management, to comply with an obligation to maintain green cover over the winter, to reduce nitrate leaching. Regulations affecting farm structure and management can be enacted at the EU, member state or regional levels. Although much important environmental legislation is now enacted at the EU level, it has to be incorporated into law at the level of the member state. This leads to variations in interpretation, supplementation and enforcement. There is a need to collate and maintain information on the regulation of farming at the member state level. This would enable the development of heuristic rules that could be used for pan-European modeling.

Atmospheric dispersion modelers are taking full advantage of the technical developments in computing to increase the resolution of their models in both time and space. The processes driving agricultural ammonia emissions are largely understood, so models of emission can be constructed that will produce estimates with the time resolution required. However, the improvement in predictive performance will be limited unless such developments are matched by improvement in the modeling of manure management and in the acquisition of data to drive them.

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Table 1. Ammonia emissions by source

Scenario	Housing	Storage	Field	Total
	% of TAN production			
1	18	4	14	37
2	18	9	19	46
3	12	3	3	18

TAN production =315 Mg year^{-1}

Fig 1. Daily ammonia emissions from a. scenario 1, b. scenario 2 and c. scenario 3.

Fig 1a

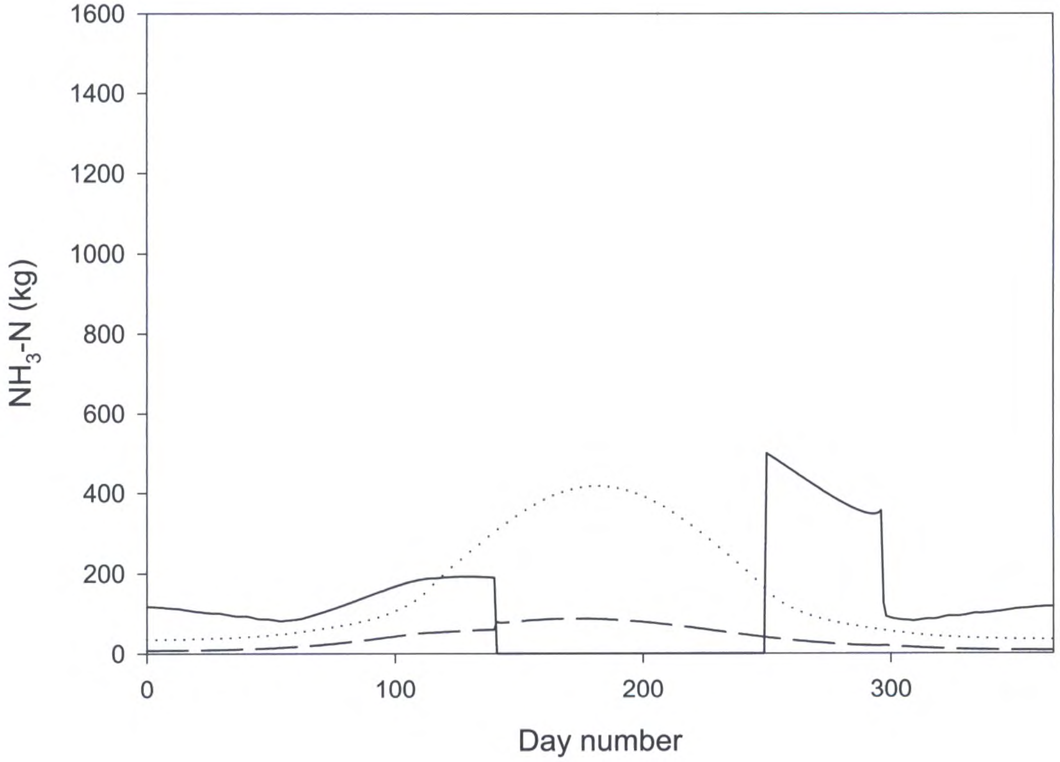


Fig 1b

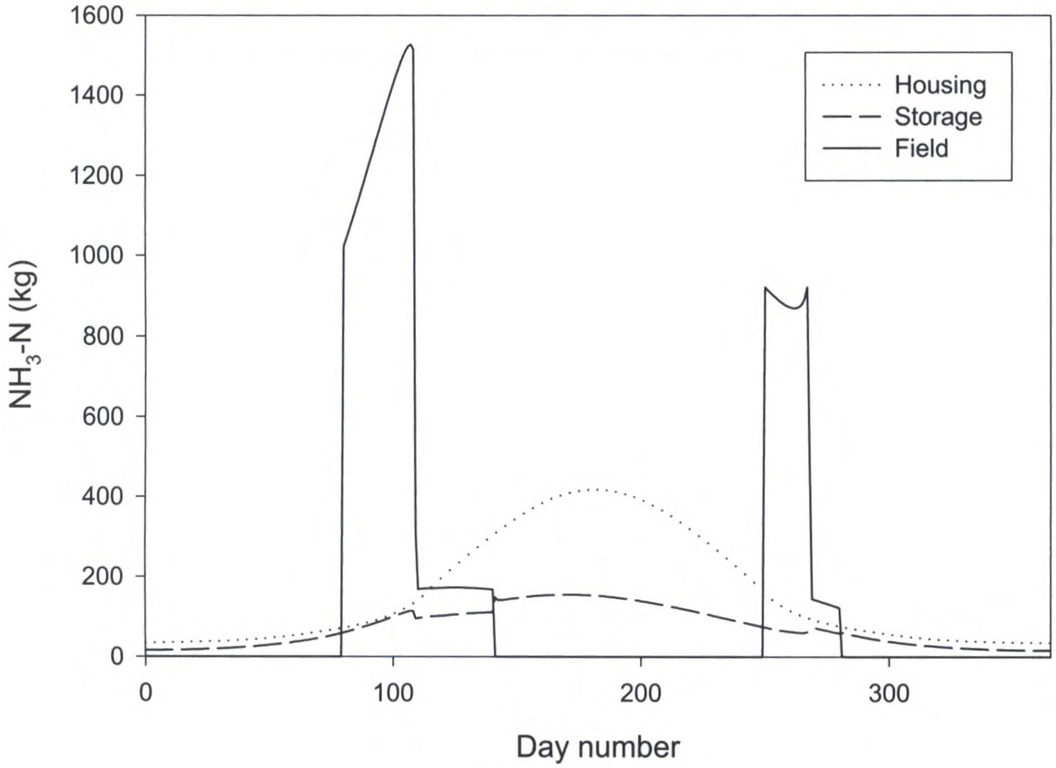
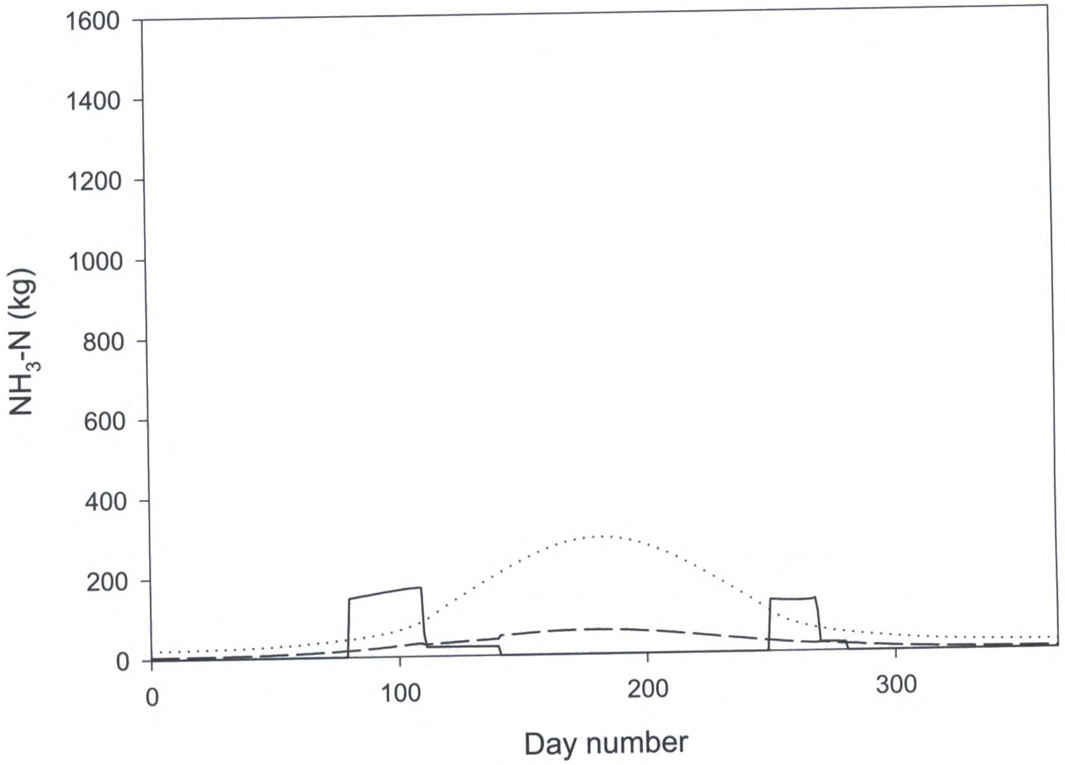

1600
1400
1200
1000
800
600
400
200
0
NH_3-N (kg)
0
100
200
300
Day number
Housing
Storage
Field

Fig 1c


1600
1400
1200
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600
400
200
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NH_3-N (kg)
0
100
200
300
Day number

International Perspectives

The Study and Regulation of Agricultural Air Quality in the U.S.

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Abstract

The livestock industry in the United States today faces two main classes of legal challenges. First, livestock odor is increasingly precipitating expensive nuisance lawsuits from annoyed citizens. Second, emissions of ammonia (NH_3), hydrogen sulfide (H_2S), and particulate matter (PM) from animal feeding operations sometimes exceed regulatory limits (either state or federal) on emissions or property-line concentrations. Both of these problems are exacerbated by increasing consolidation of livestock production.

Nuisance suits by neighbors are usually the first legal action to hit producers, and nuisance cases have been heard in nearly every livestock-producing state (Miner 1995). One key example has been the case of Iowa, where, in 1998, the State Supreme Court ruled that nuisance defense through "Right to Farm" laws was unconstitutional. By 2004, there were at least 14 separate lawsuits pending against Iowa pork producers, the most at any one time in the state's history (Lee 2004). Six years ago, a Missouri jury awarded $5.2 million to 52 neighbors for nuisance claims against a major pork-production facility owned by Continental Grain. The facility has since been purchased by Premium Standard Farms, which was itself the target of over 60 individual nuisance suits in one recent 18-month period.

Most state governments have some type of odor regulation, which goes above and beyond the nuisance concept. To regulate odor, some states use property line limits of hydrogen sulfide or odor dilutions to threshold. For example, at least 10 states have standards limiting H_2S concentrations at the property line; these are generally based on 30-minute and 24-hour averages (Mahin 2001). The 30-minute limits can range anywhere from 30 to 120 parts per billion (ppb), depending upon the state. Some state statutes limit the number of times that violations may occur before a legal action is triggered; for example, any facility which exceeds Minnesota's 30-minute 50-ppb H_2S limit more than twice in a given year can be subject to legal action. Other states have enacted limits that are dependent upon land usage patterns in the vicinity of the facility; Texas, for example, has 30-minute H_2S limits of 80 and 120 ppb, depending on land use. Several states have developed more stringent regulations to control odor and gas emissions. A prime example of this is Colorado's Amendment 14, passed by voters in 1998; it requires owners of large swine operations to obtain permits, install covers on effluent ponds, adhere to setbacks and bans on land application of wastes, and implement odor-control technologies and work practices (Sweeten et al 2001). North Carolina placed a moratorium on new hog facilities in 1997 and implemented odor rules for existing facilities in 2000. California's SB-700 legislation removed the previous agricultural exemption from state air regulations; California now will require permitting for dust, ammonia, and volatile organic compounds (VOCs).

The U.S. Department of Justice and the U.S. EPA followed Missouri and Ohio consent decrees related to odor by initiating federal actions against the same swine and layer operations for alleged excessive emissions of PM and NH_3. Both of these cases were eventually settled (in 2001 and 2004, respectively), and resulted in consent decrees with the respective producers. In the first, a Missouri pork producer with 1.25 million pigs was required, among other stipulations, to conduct long-term air emissions monitoring at two of their more than 1,000 barns, and at one of their 163 anaerobic lagoons. The producer was also required to test an approach (sprinkling of soybean oil) for controlling dust emissions. The second case involved an Ohio egg producer with approximately 12 million chickens. This producer was required by a state-issued consent decree to convert many of their deep pit barns to belt battery manure handling systems. The subsequent federal consent decree required that controls for PM and ammonia be instituted at those barns which retained the deep pit configuration, as well as long-term testing of emissions from those barns with a pair of mobile laboratories.

On the horizon are two new proposed federal rules, each of which could pose significant new challenges to the agriculture industry and that heighten the need for high-quality research into agricultural air emissions. The first of these, which was proposed by EPA on January 17, 2006 (USEPA 2006), redefines what size

fractions of particulate matter would be regulated. Existing PM_{10} standards would be eliminated, and replaced with a standard for "inhalable coarse particles", or $PM_{10\text{-}2.5}$, defined as particulate matter between 10 microns and 2.5 microns in diameter. There would be no annual standard for $PM_{10\text{-}2.5}$ in terms of concentration. The 24-hour standard would be approximately 50% lower than the current 24-hour PM_{10} standard. Significantly, any case in which the $PM_{10\text{-}2.5}$ is "dominated by windblown dust and soils and PM generated by agricultural and mining sources" would be exempted. However, the proposed rule would also lower the 24-hour $PM_{2.5}$ standard by roughly 50%, from 65 $\mu g/m^3$ to somewhere in the range of 30 to 35 $\mu g/m^3$, and there would be no agricultural exemption for $PM_{2.5}$. The second new rule, proposed November 1, 2005 (USEPA 2005), is significant in that it addresses ammonia as a precursor of PM, particularly $PM_{2.5}$. Because of this, states with nonattainment areas for $PM_{2.5}$ would be advised to assess whether reductions of ammonia emissions would assist in meeting the $PM_{2.5}$ standards. No state would be required to make this assessment unless it, or EPA, could demonstrate that ammonia emissions, in their particular case, "significantly contribute to the $PM_{2.5}$ problem in a given nonattainment area or to other downwind air quality concerns." Livestock groups, including the National Pork Producers Council (Buhl 2006) have criticized this proposed rule on the grounds that the science behind it is incomplete in two major areas: 1) understanding which fraction of ammonia emissions can be attributed to livestock agriculture, and 2) understanding fully the role of ammonia in $PM_{2.5}$ formation.

State and federal agencies have primarily relied on universities and federal laboratories to increase scientific knowledge about livestock air emissions through laboratory and field experimentation, and computer model development. They have also developed mechanisms to bring this knowledge and expertise to bear in developing sound, science-based policy. In 1997, the federal Agricultural Air Quality Task Force was established, with members from EPA, USDA, industry, and universities. The AAQTF reports directly to the Secretary of Agriculture on issues relating to the nexus between science and policy. The AAQTF issued a white paper on the livestock odor issue in 2000 (Sweeten et al 2000). AAQTF encouragement was one factor that spurred EPA to request a National Academy of Sciences (NAS) study of air emissions from livestock facilities. The report of this study, issued in 2003, highlighted possible air pollution problems arising from animal feeding operations and called for more research to address data gaps.

Methods of on-farm emission measurements have improved significantly over the past 10 years, and real-time monitoring approaches have been used to collect over 500 barn-months of air emission data since 1997, including a recently completed six-state USDA study (Heber et al 2002 a & b). The experience gained in the various monitoring studies over the last decade will now pave the way for the most comprehensive air emissions study ever conducted at agricultural facilities.

National Air Emission Monitoring Study

The National Air Emission Monitoring Study (NAEMS) is required by an innovative and voluntary Consent Agreement between the U.S. EPA and participating livestock industries. Livestock producers agreed to collect air emission data, via the NAEMS, in exchange for temporary protection from further government lawsuits and forgiveness of possible past offenses. Never before has such an air compliance program been implemented with an entire industry.

The specific objectives of the NAEMS are to:

- Determine whether individual farms are likely to emit particulate matter (PM) and volatile organic compounds (VOCs) in excess of applicable Clean Air Act thresholds.
- Determine whether individual farms are likely to emit NH_3 and/or H_2S in excess of applicable Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and Emergency Planning and Community Right-to-Know Act (EPCRA) reporting requirements.
- Form a database with which additional studies of air emissions and effectiveness of control technologies can be compared, and from which emission factors can be developed.

The NAEMS, scheduled to begin in late 2006, is designed, through the use of sound scientific principles and using proven instrumentation and methods, to provide quality-assured air emission data from representative swine, egg layer, dairy, and broiler farms. The NAEMS will employ continuous monitoring from on-farm instrument shelters to determine emissions from barns and micrometeorological methods to do the same for dairy corrals, lagoons and manure basins. In addition to collecting new data from several farms, the NAEMS will assemble and evaluate existing emissions data from other studies.

At each of one broiler site, three egg production facilites, five swine farms, and six dairies, an on-farm instrumentation shelter (OFIS) will house equipment for measuring pollutant concentrations at representative air inlets and outlets, barn airflows, operational processes and environmental variables. A multipoint gas sampling system will draw air sequentially from representative locations and deliver selected streams to a manifold from which on-line gas monitors draw sub samples. Mass concentrations of PM_{10} will be measured at a representative exhaust location in each barn using real-time monitors. Total suspended particulate (TSP) and $PM_{2.5}$ will be measured gravimetrically. Sampling of all of these parameters will be conducted for 24 months, with data logged every 60 seconds. Data will be retrieved with network-connected PCs, formatted, validated, and delivered to EPA for subsequent calculations of emission factors.

Micrometeorological techniques will be used to estimate emissions of NH_3 and H_2S from a swine manure basin, five swine lagoons, an egg layer lagoon, and three dairy lagoons. This approach will use optical remote sensing, both downwind and upwind of the storage, coupled with 3D and 2D wind velocity measurements. The concentrations of NH_3 will be determined using scanning tunable diode laser absorption spectroscopy. Measurements of H_2S and NH_3 will be conducted using UV differential optical absorption spectroscopy. A monitoring team will conduct an 11-day test at each farm each quarter for two years.

The benchmark NAEMS data, and accompanying analysis and interpretation, will allow EPA and producers to reasonably determine which farms — based on type, size, and/or geographic location — are subject to federal regulations. The database will aid environmental consultants and air dispersion modelers to assess and reduce the impact these sources have on neighbors and the environment. Policymakers, regulators, environmental groups, and producers will have increased understanding of livestock air pollution.

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Agricultural Air Quality in Europe and the Future Perspectives

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Abstract

Agricultural emissions in Europe are important to several atmospheric transport related environmental issues. These include local and regional air quality problems, such as PM exposure, euthrophication and acidification, toxics and contribution to greenhouse gas emissions, resulting in a number of environmental impacts. Over Europe, agricultural emissions are variable in space and time, and the contribution to the different issues are variable. Policies have been developed to combat some these emissions with some success. However, future, national and European policies are necessary to successfully decrease emissions and its related problems. Currently there is a move towards more integrated policies. A clear example is the nitrogen issue. Nitrogen does not only contribute to air quality, but also to water quality and to the greenhouse effect in a cascade. The efficiency of nitrogen use, especially in animal agriculture, can be increased by best management practices and/or technological innovation, resulting in much lower losses to the environment.

Introduction

European agriculture is extremely diverse, ranging from large, highly intensive and specialized commercial holdings to subsistence farming using mainly traditional practices. Consequently, impacts on the environment vary in scale and intensity and may be positive or negative. There is a legacy of significant environmental damage associated with agriculture in Central and Eastern Europe, the Caucasus and Central Asia, often associated with unique ecosystems, where exploitation of resources (such as freshwater for irrigation) was excessive. The dramatic decline in resource use in these countries, largely due to economic restructuring rather than policy, consumer or technological developments, has scaled back many environmental pressures.

A common policy objective throughout Europe for several decades was to increase food production. Farmers increased agricultural output significantly between the 1940s and the 1990s in response to such policies. Supported by public investment, this resulted in mechanization combined with the abandonment of traditional practices, reliance on non-renewable inputs such as inorganic fertilizers and pesticides, the cultivation of marginal land and improvements in production efficiency. In Western Europe (WE), the common agricultural policy (CAP) and several national policies encouraged intensification. This took various forms, including the sustained use of chemical inputs, increasing field size and higher stocking densities. Intensified farm management led to discontinuation of traditional fallowing practices and crop rotations resulting in a displacement of leguminous fodder crops with increased use of silage and maize. Specialization and intensification have resulted in a decrease in the number of farm holdings and numbers employed, as well as a rationalization of production leading to less diversity of local agricultural habitats.

Agriculture is an important sector contributing to environmental effects and more specifically air quality related issues. Air quality contributes to human health through exposure of ammonia, toxic organic compounds, pesticides, and particulates. Air quality also contributes to climate change in the form of greenhouse gases and as cooling aerosols. After deposition, eutrophication and acidification might occur and, in combination with climate change biodiversity is endangered, and the net-greenhouse gas exchange is affected. There are two ways to assess the contribution of agriculture to air quality; that is the share of agricultural emissions to the total emissions in Europe, or through the contribution of agriculture to the observed effects in Europe. The latter is less uncertain and not followed here.

Contribution of agricultural emissions

In 2002 agriculture contributed 10.1% to the total greenhouse gas emissions in CO_2 equivalents in the EU15 (EEA, 2005). The greenhouse gases emitted by agriculture are nitrous oxide and methane, both of which have a far greater global warming potential than carbon dioxide. Agriculture also consumes fossil fuels for farm operations, thus emitting carbon dioxide. CO_2 comprises only a small part of these emissions (0.05%) and N_2O and CH_4 contributed equally 4.9%. For N_2O the main source is fertilizer use and for CH_4 enteric fermentation of mainly cattle. The Kyoto target for the EU is 8% reduction in 2008-2012 relative to 1990. Emissions of greenhouse gases by the agriculture sector — methane and nitrous oxide — fell by 8.7 % between 1990 and 2002. This is due mainly to a 9.4% reduction in methane from reduced livestock numbers and an 8.2% reduction in nitrous oxide from decreased nitrogenous fertilizer use and changed farm management practices. These are the emissions from sources, but agriculture also produces indirect greenhouse gas emission, e.g., through nitrates, which are leached and run-off to surface waters and, eventually to the sea. During the transport N_2O can be emitted. The same holds for the deposition of nitrogen to nature areas, which to some extend can be de-nitrified, leading to N_2O emissions. Additional CO_2 can be sequestered as the result of nitrogen deposition and due to agricultural practices (e.g., de Vries et al., 2006). The net-emissions of greenhouse gases are, however, not yet quantified with some accuracy.

The contribution of agriculture to the total acidifying emissions in Western Europe is 31%, and 13% in Eastern Europe, for eutrophication the contribution is 24% and 20% for Western Europe and Eastern Europe, respectively. Figure 1 shows the total and agricultural emission of different components in EU15 as estimated by EMEP. By far the most important component is ammonia, which for more than 90% is determined by agricultural emissions. Within the EU-15, emissions of ammonia to the atmosphere from agriculture decreased by 9% between 1990 and 2002. The majority of this reduction is likely to derive from a reduction of livestock numbers across Europe (especially cattle), and the lower use of nitrogenous fertilizers across the EU-15 (Erisman et al., 2003; EEA, 2005).

The contribution of agriculture to the PM2.5 emissions is about 5%, and 25% for the PM10 emissions. Current investigations show that PM emissions from agriculture in intensive emission areas might contribute more than currently estimated. The gap between modeled and measured PM concentrations might for a large part be explained by an underestimate of the agricultural sources.

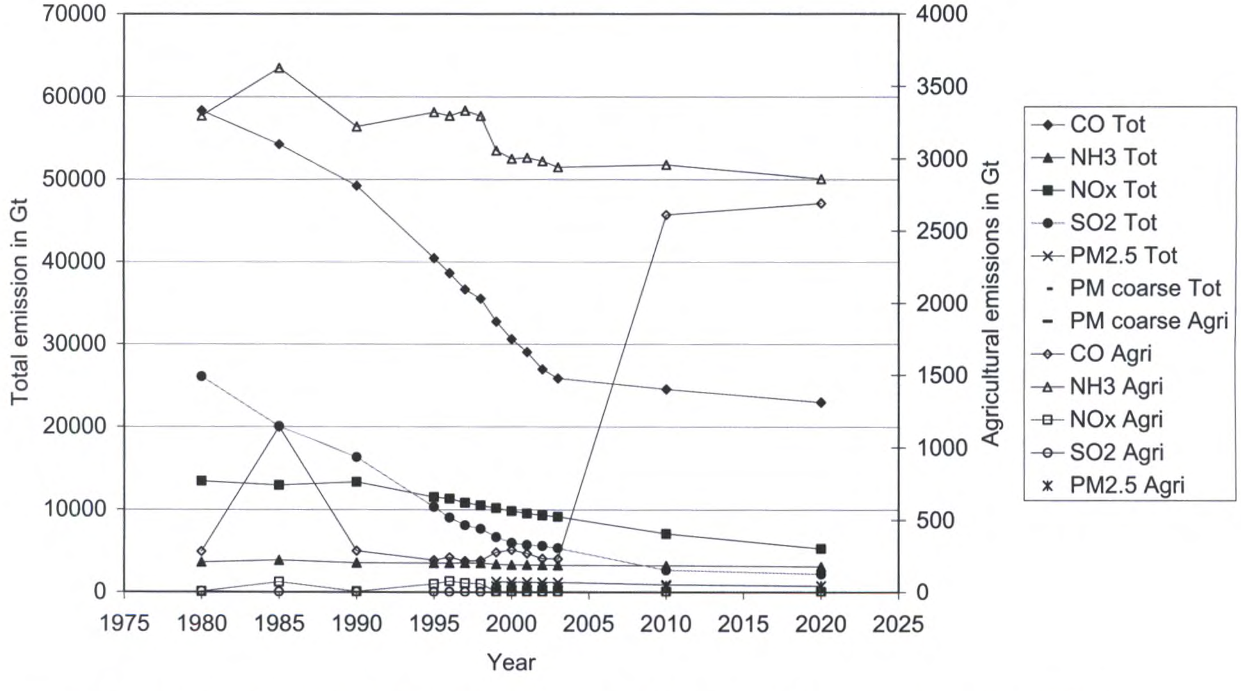

Figure 1. Trend in best estimate emissions from all sources and from agriculture in EU15 (Gt), source: http://webdab.emep.int/scaled.html

All EU-15 Member States have action plans for climate change and air quality. Most plans and programs under the National Emission Ceilings (NEC) Directive include measures to reduce ammonia emissions from agriculture due to their negative health and environmental effects. According to current projections (which exclude potential effects of the 2003 CAP reform) many member states are likely to miss their 2010 ammonia reduction target under the NEC directive. The predictions are shown in Figure 1. The agriculture sector can make a positive contribution to reducing greenhouse gases through the production of bio-energy, thus substituting for fossil fuels. Agriculture at present contributes 3.6% of total renewable energy produced and 0.3% of total primary energy produced in the EU (EEA, 2005).

The common agricultural policy has been one of the important drivers of farm intensification and specialization in the EU. Market pressures and technological development have also contributed to these trends, which are very strong in some sectors that benefit from little public support (e.g., pigs, poultry, potatoes). Intensive farming has had significant impacts on the environment. Public concerns related to production methods and some reorientation of the common agricultural policy has created new opportunities, for example through labeling and agri-environment schemes, for farmers to reduce pressures on the environment. Agriculture in the Central and Eastern Europe countries is likely to intensify when they have full access to the common agricultural policy, although there is an evolving agri-environmental policy framework and some opportunities under the special accession program for agriculture and rural development to address this risk. The common agricultural policy will apply to new member states in a modified form, which may reduce incentives for increasing production.

Future Focus

Erisman et al. (2005) made an overview of the effectiveness of policies in the Netherlands and Europe to reduce nitrogen emissions. The main conclusion is that policies should not be focused on increasing production alone rather than including the farm nutrient efficiencies. Through the focus on production, combined with the low cost of e.g., concentrates and fertilizers, the efficiency of nutrient cycling at the farms has been neglected. Measures include taxes or financial grants, and the targets setting for N losses. Furthermore, the closing of cycles should be done at different scales at the same time. We are accustomed to seek our improvements in technological options. There are potential technologies that might lead to substantial emission reduction (catalytic converters, hydrogen economy, nitrification inhibitors, fermentation of manure, etc.). These are important, but the reduction in environmental load they cause should not lead to increased import of raw materials, leading to changes in cycles at supranational scales. Furthermore, other components (such as carbon) and issues (access to freshwater) should be taken into account to prevent trade-offs. If financial incentives are given, it is important to secure the period that these incentives will last, in order to guarantee a return of investment.

The largest uncertainty in emission estimates is due to the diffuse sources and the generalisation of the different sources, varying in space and time. New methods are developed to measure accurately and with enough temporal resolution the ambient concentrations. This is necessary to improve the quantification of individual sources and the regional sources. The landscape scale is so far not well quantified. Major uncertainties rest in the local and regional ammonia emissions and its temporal variation and in the PM emissions from agricultural sources.

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Air Quality and Agriculture: The Role of Global Drylands and Arid Zones

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Abstract

The available information on trace gas exchange of CH_4, CO, N_2O, NO_x, and VOCs arising from agriculture and natural sources in the world's drylands and arid zones due to soil and plant processes is reviewed.

Together, the semi-arid and semi-humid zones, called the drylands, cover about 30% of the global land area, and a further 17% of the global land area are in the hyper-arid and arid zones. More than a third of the world's human population live in these arid and dryland regions. The vegetation and soils of these arid and dryland regions are fragile and are prone to desertification, particularly through the loss of soil nutrients, soil organic matter and the invasion of woody shrubs.

The contribution of these drylands and arid zones to the global cycles and budgets of trace gases, and the changes to these contributions effected by land use modifications in these regions, have not been extensively researched. Between 10 and 40% of the global soil-atmosphere exchange for these gases (CH_4, CO, N_2O, NO_x, and VOCs) may occur in these zones, but for most of these gases there are less than a dozen studies to support the individual estimates. Signficant differences are identified in the biophysical and chemical processes (production and diffusion) controlling these trace gas exchanges between dryland and arid zones and other land regions, and are not well represented in the current global models of trace gas emissions. Therefore, we have a poorly quantified understanding of the contribution of these regions to the global trace gas cycles and atmospheric chemistry. More importantly, we have a poor understanding of the feedbacks between these exchanges and global change and regional land use and air pollution issues. A challenge exists to aquire more data on trace gas exchange from these zones and for models to be extended to incorporate those processes that are special for trace gas exchange to the dryland and arid zones.

Introduction

Human changes to the Earth's biosphere have profoundly changed the concentrations of climatically-active and other trace gases in the Earth's atmosphere. The atmospheric effects of deforestation and the expansion of ruminant animal numbers, as well as some other changes to the biosphere, are well quantified. In other cases, such as the loss of vegetation and soil organic matter from unsustainable use of drylands, the atmospheric consequences are poorly understood. The purpose of this paper is to review and analyse the contribution of agriculture and natural processes in the world's drylands and arid zones to global and local air pollution problems via soil-atmosphere exchange.

There are two ways of classifying arid, semi-arid and dryland areas. One is based solely on preceipitation (P), and the other on the ratio of precipitation to potential evapotranspiration (PET). Under the first approach, arid and semi-arid regions have an annual precipitation of less than 300-400 mm. Under the second approach, the ratio of P/PET which is called the "degree of aridity" (UNESCO 1977) is used. It should be noted that this is a climatological land classification. Within any of these zones, the full range of land cover types from barren to forest can potentially occur, although, naturally, shrub land and sparsely vegetated land cover prevail in the arid zone. Similarly, there is a separate range of land uses.

The definitions of these areas, the areas covered as a fraction of the global land area and the populations of these areas are summarised in Table 1. Together, the semi-arid and semi-humid zones, called the drylands, cover about 3.8×10^9 ha globally, or about 30% of the global land area (Leemans and Kleidon 2002), and a further 17% of the global land area is in the hyper-arid and arid zones, subsequently described as the arid zones. More than a third of the world's human population live in these arid and dryland regions.

The vegetation and soils of these arid and dryland regions are fragile and are prone to desertification, particularly through the loss of soil nutrients, soil organic matter and the invasion of woody shrubs (Leemans and Kleidon 2002). The contribution of these dryland and arid zones to the global cycles and budgets of trace gases and the changes effected by land use modifications in these regions have not been extensively researched and are poorly quantified and not adequately represented in models of these exchanges.

Table 1. Areas and populations of the world's arid and drylands (UNDP/UNSO 1997)

Zone	Hyper-arid	Arid	Semi-arid	Dry sub-humid
P/PET	≤0.03	0.03 – 0.2	0.2 – 0.5	0.5 – 0.75
Area 10^6 km	9.4	15.9	23.7	13.9
% of global land area	7	12	18	10
% of global population	-	4	16	18

Trace Gas Exchange in the Drylands and Arid Zones

A summary of observations and models of trace gas exchange from dryland and arid land systems is reviewed and discussed, each gas separately. Data from an unpublished year-long field study of mature Mallee vegetation and a nearby wheat crop in the semi-arid zone in Australia, (34.5°S, 141.5°E), conducted by the authors (Galbally et al. 2006) is included in the review. In preparing this review, the authors have attempted to identify all the relevant literature, although no doubt some papers have been overlooked. When considering the semi-arid zone, studies from sites with precipitation less that 400 mm per annum are included. Studies with less that 2 weeks field data have been omitted. Where data from dryland and semi-arid zone studies have been used in summaries in the review and not explicitly acknowledged in the text, the reference is included and followed by an asterisk.

Methane

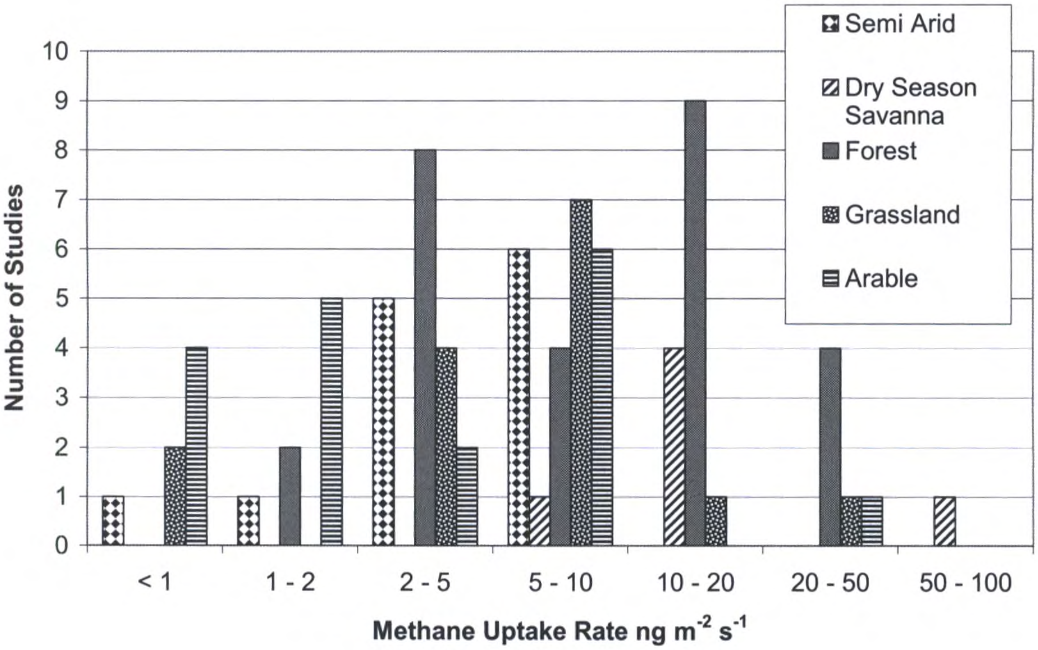
Methane (CH_4) is a potent greenhouse gas, and its abundance in the atmosphere makes it a significant component of the global carbon cycle. Globally, soils are a significant sink for methane and account for a global annual uptake of 30 Tg y^{-1} (IPCC 2001). The factors affecting methane exchange in desert, semi-arid and seasonally dry lands are somewhat different from those controlling methane exchange in temperate systems, including the complicating factor of the significant activity of soil invertebrates, particularly termites, which produce methane as a byproduct of cellulose digestion. Under very dry conditions, with soil moisture below 5% water filled pore space (WFPS), methane uptake is near zero (Striegl et al. 1992, Otter and Scholes 2000). At moderate soil moisture levels, both uptake and emission of methane occur (Poth et al. 1995, Anderson and Poth 1998, Otter and Scholes 2000, Verchot et al. 2000). The switch between the methane uptake and emission can be associated with the burning of above-ground vegetation (Poth et al. 1995, Anderson and Poth 1998). The explanation of this phenomenon is that there is extensive methane production by foraging subterranean termites and that these emissions counterbalance the soil methane uptake. Burning of the above-ground biomass removes the food source for these termites, reduces emissions and tips the balance in favour of methane uptake. Other processes, such as cultivation or harvesting or overgrazing the above-ground vegetation, will presumably have the same effect in reducing the termite component of methane emissions.

In the semi-arid shortgrass steppe of southwestern United States, cultivation and nitrogen fertilization reduced methane uptake (Mosier et al. 1991, Mosier et al. 1996). In the swamps and wetlands of seasonally wet savannas, the transition to higher WFPS and higher root or microbial respiration can promote anaerobic conditions in the soil and increase methane emissions from fermentation (Otter and Scholes 2000, Verchot et al. 2000).

We have gathered the methane uptake rates from the five available extended studies in semi-arid regions, and find an average methane uptake of 5.6 ± 2.9 ng (C) m^{-2} s^{-1}, (range 1-10). Similarly we have gathered the methane uptake rates for the eight available extended studies from the dry season in seasonally wet/dry savanna sites. During the dry season, when only 5-15% of the annual precipitation occurs, the average methane uptake rates are 12 ± 20 ng (C) m^{-2} s^{-1}, (range -10 to 60) where the negative uptake is an emission. In the wet season for seasonal wet/dry savanna, methane emission frequently dominates methane exchange. These uptake rates for the dry season in savanna are higher than those of the semi-arid region, perhaps because the wet/dry seasonal cycle keeps the soil more moist, and the methanotrophic bacteria more active.

We present the methane uptake rates for dryland and arid systems in Figure 1, along with existing estimates for other regions (Smith et al. 2000; Boeckx and van Cleemput 2001). It is clear from Figure 1 that the methane uptake rates in semi-arid regions are small compared to those in other systems throughout the world, but because of the large area of the arid and dryland zones, see Table 1, as much as 40% of the soil sink for methane may occur in drylands and arid zones where little data exists.

Figure 1. The rates of methane uptake in different systems Units ng (C) m^{-2} s^{-1}. (This study, Smith et al. 2000, Boeckx and van Cleemput 2001).



The paucity of data for this significant uptake of methane in drylands and arid zones has been commented on also by Potter et al. (1996) and Smith et al. (2000). The processes controlling the methane uptake in drylands and arid zones are soil moisture and soil microbial activity, subterreanean termites, above-ground biomass and its loss through burning, drought, grazing and harvesting. It is a challenge for current models that incorporate methane exchange to include these processes. An even greater challenge is to understand how microbial community structure might change in response to other environmental changes and affect global soil-atmosphere trace gas exchange including methane (Schimel and Gulledge 1998). If climatic boundaries change (as is suggested by the IPCC (2001), then there will be a feedback through changes in the global methane uptake rate. More critical experimental studies and developments in techniques for modelling of these soil exchange processes will be necessary to quantify and model that feedback of methane uptake in arid and dryland zones.

Carbon Monoxide

Carbon monoxide (CO) plays important roles in the atmosphere through its reaction with hydroxyl radicals (Levy 1971) and its ozone-forming potential in NO_x-rich environments (Crutzen and Zimmermann 1991). Both of these processes lead to the oxidation of the carbon monoxide to carbon dioxide.

Carbon monoxide is produced in the soil through the thermal and photochemically induced oxidation of humic acids and phenolic materials that are present in the soil and by the decomposition of cellulose, particularly in dead above-ground biomass (Conrad and Seiler 1985a & b, Schade et al. 1999). The production of CO is positively correlated with the amount of dead above-ground biomass and the organic carbon levels in the soil, and its emission increases exponentially with temperature (rising markedly at temperatures above 35°C). Production of CO increases with sunlight, particularly at UV wavelengths, but is unaffected by soil moisture at low to moderate soil moisture contents (Conrad and Seiler 1985a & b, Tarr et al. 1995; Zepp et al. 1996; Schade et al. 1999; Gödde et al. 2000). For these reasons the global drylands and arid zones are potentially the major regions for soil emissions of CO.

Carbon monoxide in the soil can be utilized as a substrate by soil microbes, so that there may be CO uptake. A number of authors have demonstrated CO uptake in the field in drylands (Conrad and Seiler 1982; Conrad and Seiler 1985a & b; Scharffe et al. 1990, Sanhueza et al. 1994). This CO uptake does not vary substantially with temperature and does become more active in the transition from a dry to a moist soil.

These processes of CO production and uptake compete. Because the CO production increases with higher temperatures and CO uptake does not, there is an observed strong diurnal variation of CO exchange, with uptake at night and emissions during the daytime (Scharffe et al. 1990, Sanhueza et al. 1994).

Sanhueza et al. (1994) found that there was relatively little variation between the wet and dry seasons, although enhanced emissions were observed after heavy rains. In the Australian semi-arid study (Galbally et al. 2006), where there is a significant seasonal cycle of temperature and solar radiation, low daytime CO emissions were observed in winter and high daytime CO emissions were observed in summer.

Sanhueza et al. (1994) recorded an increase in emissions of up to 18 ng(C) m^{-2} s^{-1} from grassland from which the trees had been removed and which had been regularly mown. Interestingly, when part of the native grassland was cultivated and sown to arable crops, the site became a net sink for CO of -3.2 ng(C) m^{-2} s^{-1} during the first weeks following ploughing. Later in the season, it reverted to a net CO source (Sanhueza et al. 1994). The Southeastern Australian wheat field and the undisturbed Mallee measurements (Galbally et al. 2006) are amongst the highest CO emissions observed with yearly averaged daytime emissions of 11 ±18 ng(C) m^{-2} s^{-1}, and these emissions behave according to the same temperature dependence observed by Scharffe et al. (1990). During the daytime, from these observations, the CO emissions are equivalent to 0.1% of the carbon lost from the soil by soil plus root respiration.

Globally, CO emission from soils and above-ground dead plant material is estimated to be 100 (50 – 170) Tg CO yr^{-1} (Schade and Crutzen 1999) occurring particularly in the tropical regions including savannas, grasslands and rainforests. Soil uptake of CO is estimated to be 190 – 580 Tg CO yr^{-1} (King 1999), although a much lower estimate is made by Potter et al. (1996). Land use change and climate change affect the amount of above-ground dead biomass, the solar radiation and air temperature, and thereby the CO emission. These processes are essential ingredients for understanding and modelling CO exchange and atmospheric chemistry in the lower atmosphere (Schade and Crutzen 1999), particularly for the lower atmosphere in the drylands and arid zones. Schade and Crutzen (1999) call for more measurements as well as modeling efforts to improve our understanding of CO exchange in tropical savanna, grassland and rainforest ecosystems.

Nitrous Oxide

Nitrous oxide (N_2O) is an important greenhouse gas and a key component of the global nitrogen cycle. In the soil, nitrous oxide is produced predominantly through the conversion of forms of nitrogen, such as ammonium and nitrate, by soil bacteria (Bremner 1997). Nitrous oxide (and nitric oxide) are gaseous intermediates of both processes. The microbial processes of nitrification and denitrification account for about 99% of the nitrous oxide generated in the soil ecosystem (Webster and Hopkins 1996). Because nitrous oxide is an intermediate in these processes, its emission is not quantitatively linked to the masses of ammonium or nitrate substrates (either available or transformed).

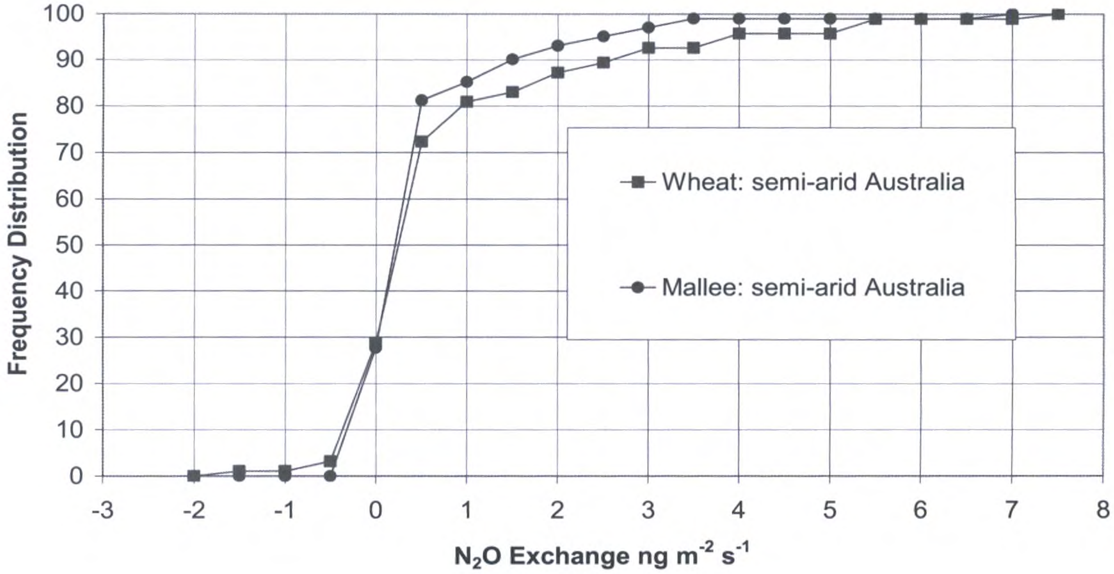
Both ammonium and nitrate are important plant nutrients and are commonly applied to the soil as fertiliser to encourage plant growth. However, these ions are also essential substrates for nitrifying and denitrifying bacteria. It is not surprising, therefore, to find that much of the literature related to nitrous oxide emissions is involved with the relationship between fertiliser application and nitrous oxide (or nitric oxide) emission (Matson et al. 1998). The rates of microbial activity, and hence both nitrification and denitrification, increase with increasing temperatures. Although temperature optima vary with bacterial species, the optimum temperature range for nitrification is 25°C to 35°C, with a somewhat higher temperature optimum for denitrification (Granli and Bøchman 1995).

In hot dry climates, the addition of fertiliser has little impact on the concentration of soluble nitrogen or on emission of nitrous oxide (Matson et al. 1998). However, when the soil is moistened (either through rainfall or irrigation) ammonium levels increase dramatically, and then decrease to nearly zero as the proliferation of nitrifying bacteria under the moist conditions convert the ammonium to nitrate and releases nitric and nitrous oxides (Mummey et al. 1994, Matson et al. 1998, Wulf et al. 1999). The production of nitrous oxide from nitrification upon wetting of dry soil happens with a rapidity and intensity that is not characteristic of temperate agricultural systems. (A similar phenomena is observed with CO_2 respiration in hot dry soils by Xu et al. (2004)) Also, in spite of semi-arid soils being substantially aerobic, there is a persistent pool of denitrifying enzymes that are able to survive the drought and become activated rapidly after the soil becomes wet, provided there are sufficient carbon and nitrogen substrates available in the soil (Peterjohn 1991).

A study of Mexican wheat fields, by Panek et al. (2000), indicated that, following irrigation, denitrification accounted for most of production of nitrous oxide, but as the soil dried out, nitrification became predominant. Over the growing season, the nitrous oxide flux was influenced almost equally by the two processes. In Australian grazed pasture, emission from nitrification accounted for more than 50% of annual total emissions (Wang et al. 1997). In Figure 2, the cumulative frequency distributions of N_2O emissions from the Australian study (Galbally et al. 2006) are presented. As can be seen from the distribution of individual measurements in the Australian study, the highest 5% of the observations (those greater than the 95 percentile) are around 10 times or more than the median emissions. These high emissions correspond to the few rain events but over the year contribute around half of the total emissions.

There are nine comparisons of nitrous oxide emissions from farmed versus natural vegetation in semi-arid regions, and these indicate a net extra contribution from cultivation to N_2O emissions of 0.1 kg N ha^{-1} y^{-1} (Parton et al. 1988, Mosier et al. 1991, Mosier et al. 1996, Corre et al. 1996; Mosier et al. 1997; Guilbault and Mattias 1998, Huang et al. 2003, Galbally et al. 2006). Due to the large areas involved, this may represent as much as 10% of the global soil emissions of N_2O from agricultural disturbance may occur in drylands and arid zones where little data exist. There are more than 800 studies of nitrous oxide emissions from agricultural systems (Bouwman et al. 2002) and only nine of these are from the extensive semi-arid zone. (The global emissions are drawn from IPCC (2001). The processes controlling the N_2O emissions in drylands and arid zones that occur on re-wetting of dry soil as well as denitrifying enzymes that are able to survive the drought and become activated rapidly after the soil becomes wet are not characteristic of the temperate zone. Current models of N_2O emissions from soils (Wang et al. 1997, Frolking et al. 1998, Parton et al. 2001) do not have these processes explicitly included. A consequence is that, if climatic boundaries change (as is suggested by the IPCC (2001), then there will be a feedback through changes in the global N_2O emissions; but we cannot quantify or model that feedback because of the lack of understanding of N_2O emission processes in arid and dryland zones.

Figure 2. The cumulative frequency distributions of N_2O emissions from the Australian study (Galbally et al. 2006).



Nitric Oxide and Nitrogen Dioxide

Nitric oxide (NO) and nitrogen dioxide (NO_2) are of importance due to their roles in the nitrogen cycle and in the acidification and ozone levels of the atmosphere (Crutzen 1979). The chief sources of nitric oxide in soils results from the action of denitrifying and nitrifying bacteria and the chemical decomposition of NO_2^- under acidic conditions (Firestone and Davidson 1989), although on a global scale, the latter process is of only minor significance (Galbally 1989). While there are many observations of NO emissions from tropical savanna, the database from semi-arid regions is sparse. At the time of the inventory of global emissions studies by Davidson and Kingerlee (1997), there were no published and one unpublished study from desert regions. Subsequently there have been a number of studies in semi-arid zones (Le Roux et al. 1995, Smart et al. 1999, Hartley and Schlesinger 2000, Barger et al. 2005, Galbally et al. 2006).

In dryland and semi-arid systems, where soils are well aerated, nitrification is expected to be much more important for the production of nitric oxide than denitrification. Soil moisture is a critical factor in determining the rate of nitric oxide emission. Following the wetting of dry soils, nitric oxide emissions are rapidly increased by about one order of magnitude, and then decays to original levels over the next few days (Johansson et al. 1988, Rondón et al. 1993, Levine et al. 1996, Scholes et al. 1997, Meixner et al. 1997, Smart et al. 1999, Hartley and Schlesinger 2000, Pinto et al. 2002), probably due to increases in microbial activity and in the rate of diffusion of NO in the moist aerated soils (Davidson et al. 1993, Cárdenas et al. 1993). However, as soil moisture approaches field capacity, NO emissions from nitrification decrease due to the restriction in oxygen diffusion (Bollman and Conrad 1998). The temperature dependence of NO emissions is quite weak in semi-arid and arid regions, where soils are drier (Stocker et al. 1993) or where temperatures may be above the optimal temperature for microbial activity (Cárdenas et al. 1993). Ludwig et al. (2001) suggests that soil temperature is best considered as "a factor that mainly modulates short-term variation of the NO exchange, whereas the magnitude of NO emissions is predominantly controlled by other factors." The presence of termites in the soil leads to higher than normal emissions of NO, possibly due to enhanced NO_3^- concentrations in the termite mounds (Rondón et al. 1993, Le Roux et al. 1995).

The four longer term studies from the semi-arid zone indicate average NO emissions in the range 0.1 to 1.8 kg N ha^{-1} y^{-1} with the higher value coming from the Sahel ((Le Roux et al. 1995, Smart et al. 1999, Hartley and Schlesinger 2000, Barger et al. 2005). These four studies indicate that the semi-arid lands (as well as the tropical savannas) are a major contributor to soil NO emissions. This has been borne out by the satellite sensing and inverse modeling study of Jaeglé et al. (2004) who observed strong pulses of soil NO emissions lasting 1-3 weeks after the onset of rain in the semi-arid sub-Saharan savanna. Jaeglé et al. (2004) extrapolated this finding to all of the tropics and estimated a 7.3 Tg N yr^{-1} biogenic soil NO source, perhaps 20% of the global NO_x emissions. So far neither this NO pulse following re-wetting of dry hot soils nor termite activities are included in process based models of NO emissions. Recently a statistical model of NO emissions (Yan et al. 2005) has developed an empirical methodology to include this NO pulse activity. There is a need for more surface based critical studies of NO emissions in the semi-arid zone to confirm the satellite observations of Jaeglé et al. (2004), and to provide the experimental basis so that process models may be extended to include this re-wetting pulse phenomena that significantly affects the soil atmosphere exchange of NO, N_2O and CO_2.

Volatile Organic Compounds

The volatile organic compounds emitted from plants (BVOCs) play a significant role in atmospheric processes including ozone production and the formation of secondary aerosols (Monson and Holland 2001, Atkinson and Arey 2003). As a consequence of their emission, BVOCs influence the global carbon cycle, the Earth's radiation balance and the distribution of reactive gases such as carbon monoxide and organic acids (Guenther et al.1999).

Numerous BVOC are emitted from vegetation, but on a global scale, isoprene and monoterpenes are the most commonly investigated because of their high relative abundance and their high chemical reactivity, and trees are the major source. Guenther et al. (1995) estimated a global BVOC annual budget of 1150 Tg(C) y^{-1}, an amount comparable to the global emission of methane. Of this budget, isoprene and monoterpenes contributed 44% and 11%, respectively. Grass species are, in general, low emitters of isoprene and monoterpenes (Hewitt and Street 1992), and instead emit mainly low molecular weight oxygenated compounds such as methanol, acetone, and acetaldehyde (Kirstine et al. 1998).

The emission rates of BVOCs vary markedly with plant species and also with leaf age and past environmental conditions, making the ecosystem emissions of BVOCs quite variable (Guenther et al. 1999). Since the emission of BVOCs increases with temperature (and in some cases with solar radiation), semi-arid biomes in tropical or temperate regions have a high potential for BVOC production (Guenther et al. 1996).

Tropical savannas are semi-arid mixed tree-grass ecosystems that cover about one-half of the areas of Africa, Australia, and South America and cover one-eight of the Earth's total land area (Scholes and Archer 1997). For savannas (as for other grassland ecosystems) most of the isoprene and monoterpene emissions result from trees and shrubs that occur within these landscapes. For central African savannas, Otter et al. (2003) determined summer time isoprene emissions of 5.1 mg(C) m^{-2} h^{-1} for wooded savannas and 1.7 mg(C) m^{-2} h^{-1} for grass savannas. Winter emissions were about a factor of four lower. Summer time emissions of monoterpenes in wooded savannas were generally in the range of 0.1-0.3 mg(C) m^{-2} h^{-1}, although emission rates from mopane woodlands (dominated by *Colophospermum mopane*) were much higher, at approximately 2.0 mg(C) m^{-2} h^{-1} (Otter et al. 2003). These measurements are consistent with those of other investigations of BVOC emissions from African savannas (Guenther et al. 1996, Klinger et al. 1998, Guenther et al. 1999, Otter et al. 2002). In a study of VOC emissions from savannas in southern Africa, Otter et al. (2002) calculated annual emission rates of 1.9 to 9.3 g(C) m^{-2} y^{-1} for isoprene and 0.7 to 1.7 g(C) m^{-2} y^{-1} for monoterpenes. If these estimates are taken to be representative of the drylands of the world, which have a global area of 28 x 10^6 km^2, the total production of isoprene from savanna ecosystems is 130 ± 90 Tg (C) y^{-1}, and the total production of monoterpenes is 28 ± 11 Tg (C) y^{-1}.

Grasslands are undoubtedly a significant global source of methanol (Galbally and Kirstine 2002) and acetone (Jacob et al. 2002). A study of VOC emissions from grass pasture in Australia by Kirstine et al. (1998) found that about 0.25% of the carbon fixed by NPP in the pasture was lost as BVOCs. Given a global annual NPP for perennial grasslands and savannas of 42.5 Pg y^{-1} (Field et al. 1998), this conversion factor predicts a release of over 100 Tg(C) y^{-1} of BVOCs, of which about 15 Tg y^{-1} would be methanol. Grasslands are also a significant potential source of a group of C_6 aldehydes and alcohols — so-called hexenyl compounds — that are produced by grass cutting or grazing (Kirstine et al. 1998, de Gouw et al. 1999). Unlike other BVOCs, these hexenyl compounds are emitted only when the plant leaf is wounded, and their emission rate declines rapidly to zero within a few hours of the wounding. Nonetheless, these compounds are of comparable reactivity to isoprene (Arey et al. 1991) and hence have an equal potential to contribute to tropospheric photochemistry (Kirstine and Galbally 2004). While harvesting of hay crops has been shown to contribute a very minor fraction of the total global emissions of BVOCs (Karl et al. 2001, Warneke et al. 2002), the potential emission of hexenyl compounds through grazing or the trampling of animals has, to date, not been estimated.

The above estimates indicate that 25% of the global BVOC emissions may come from the world's drylands, based on a few studies. The mechanisms of BVOC emissions vary markedly with plant species and also with leaf age and past environmental conditions, and these are not the same in the drylands as in temperate regions. Our ability to understand and model the role of volatile organic compounds emitted from plants (BVOCs) in atmospheric processes including ozone production and the formation of secondary aerosols and the consequences for the global carbon cycle, the Earth's radiation balance and the distribution of reactive gases is limited by this paucity of understanding.

Conclusions

The gases considered in this review, CH_4, CO, N_2O, NO_x, and VOCs arising from agriculture and natural sources due to soil and plant processes in the worlds drylands and arid zones and their products through atmospheric chemical transformations, are important contributors to (a) the climate and radiation balance of the atmosphere (through gaseous infrared absorbance and scattering of solar radiation), (b) the chemistry and oxidising power of the troposphere through photochemistry and ozone production, and (c) to regional air quality issues through ozone and aerosol. The exchanges of these gases in the drylands and arid zones have been shown to make up 10 to 40% of the global exchanges of these gases from these land based sources and sink, yet these estimates are based in each case on a handfull of studies. More importantly, we have a poor understanding, quantification and modelling capability for some of the processes that affect these soil-atmosphere trace gas exchanges including:

- The interaction of above-ground biomass, soil invertebrate activity and soil microbial activity;
- The change of soil microbial community structure and its effect of trace gas exchange in response to other environmental change;
- The processes of decay of dead above ground biomass under high solar radiation and temperature conditions and the consequent release of trace gases including CO and VOCs;
- The soil microbial processes associated with the pulse phenomena, when on re-wetting a dry hot soil there are significant increases in the soil-atmosphere exchange of NO, N_2O and $CO_{2;}$
- The BVOC exchange of dryland and arid zone vegetation.

Furthermore there are larger scale couplings not addressed in this review, including the effects of rainfall and fire, drought and soil erosion on these dryland and arid zone exchanges that need further understanding.

New knowledge is necessary to understand how human activities and climate change may affect these dryland and arid zone exchanges and to model the feedbacks between these exchanges and global change and regional land use and air pollution issues.

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Role of Agricultural Ammonia Emissions in Formation of Secondary Particulate Matter

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Introduction, Sampling and Study Area

In a broad sense, out of pollutants monitored under National Air Quality Monitoring Program in India, there are two major issues of air quality: (i) consistently high particulate mater (PM) levels and (ii) consistently rising levels of oxides of nitrogen (NO_x). The levels SO_2 in India have dropped considerably after the introduction of low sulfur diesel (less than 0.25% sulfur) in the year 2000 (CPCB 2001). PM has been widely studied in recent years due to its potential health impacts and need for its control (e.g. Schwartz et al 1996). To understand the health effects and formation/emission of PM, it is essential to know physical characteristics and chemical composition of particles. The main components of $PM_{2.5}$ (particle with aerodynamic diameter of less than 2.5 micron) are organic matter (30-60%), metals (<1%), nitrates and sulfates (25-35%), elemental carbon (5%) and rest others (USEPA, 1995).

As seen, the major contribution to $PM_{2.5}$ is from nitrates and sulfates which are result of hundreds of reactions that take place in the atmosphere (Seinfeld and Pandis, 1998). The primary precursors for formation of nitrate and sulfate are NH_3, SO_2 and NO_x. In other words, levels of PM and NH_3, SO_2 and NO_x are interlinked through atmospheric reactions to a large extent. It has been established that most of the reactions are inorganic in nature (for formation of sulfate and nitrate), complex, and competing with each other. These reactions mostly depend on solar insolation, temperature, humidity, and presence of other constituents in the atmosphere (Utsunomiya and Wakamatsu, 1996). These parameters are location specific and show seasonal and diurnal variations, and one needs to study/measure these parameters at local and regional level.

NO_x is mainly emitted in the atmosphere as NO, which is subsequently chemically transformed into NO_2 and then into gaseous (HNO_3) and/or particulate nitrate. NH_3, emitted through agriculture and industrial activities, plays an important role in neutralizing the atmospheric acids. This neutralization occurs predominantly in aerosols, a compound system that includes ammonia, sulfuric acid, nitric acid, and water to form nitrates and sulfates.

The primary objective of the study was to understand the role of NO_x, NH_3, SO_2, HNO_3, temperature and humidity in formation of particulate sulfate and nitrate. The study area was city of Kanpur (latitude 26° 26' N and Longitude 88° 22' E), India. Specifically, the study was designed to measure the atmospheric levels of NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, NO_3^-, SO_4^{2-}, Cl^-, NH_3 (gas), HNO_3 (gas), NO_2 and PM_{10} covering winter and summer seasons and day and night samplings to capture the diurnal variations at two locations.

Results and Discussion

Results show NO_3^-, SO_4^{2-}, NH_4^+, K^+ levels are found to be significantly high in winter season compared to the summer season. In summer conditions (high temperatures and low relative humidity), particulate ammonium nitrate is volatile, and there will be less particulate nitrate. On the other hand, wintertime nitrate levels were statistically higher. The role of NH_3, which is a precursor for formation of NH_4NO_3, was very critical as nitrates under all conditions correlated with NH_4^+. The results of sampling suggested that the possible source of NH_3, at a relatively clean site (upwind of an urban area), could be from agricultural activities in rural areas in the upwind. There are three possible sources of NH_3 that can influence the atmospheric ammonia levels at a site, these include: (i) application of urea in the fields, (ii) decomposition of agricultural waste which convert organic ammonia to gaseous NH_3, and (iii) decomposition of waste from cattle population. In rural areas of India, cattle provide basic livelihood and are still employed to plough fields, as a result, India has one of the largest cattle populations in the world.

In summer time, NH_4^+ levels were significantly less (than winter levels) that suggests equilibrium shift towards NH_3 (gas) due to high temperature (>38 °C); as a result, the nitrate levels in summer will remain in gaseous form as HNO_3. As regards diurnal variation in summer, the nighttime levels of NH_4^+ were higher than daytime levels. As the temperature drops in nighttime, there may be equilibrium shift from NH_3 to NH_4^+ in presence of higher humidity resulting in higher levels of SO_4^- and NO_3^-.

In winter, mainly NO_3^-, SO_4^{2-}, NH_4^+ ions show significant diurnal variations, with higher values in daytime. In the daytime, the production of gaseous precursor (HNO_3) is found to be higher due to photochemical oxidation of NO_2 by OH radical than night time levels, when aqueous chemistry appears to dominate.

In addition to role of agricultural ammonia, potassium ions were found significantly high in the winter month (3.5±2 $\mu g/m^3$) compared to summer (1.8±.9 $\mu g/m^3$). This high level of potassium is attributed to agricultural biomass burning and guttation process, which are dominant in winter season in the agricultural areas.

This study also concluded that daytime nitrogen conversion ratio (total nitrate to NO_2 + total nitrate) was quite high at 45-52% in both the seasons. This suggests the current level of NO_x may not fully explain the problem of NO_x pollution and one must account for NO_3 conversion and examine the health implications of higher NO_3 (in form of HNO_3 and/or particulate nitrate) through a comprehensive analysis.

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Has Livestock Introduction Changed Nitrogen Openness in Southern South America?

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Abstract

In grasslands of Argentina and Uruguay a large fraction of N stored in the vegetation is consumed by domestic herbivores introduced by European settlements 500 years ago, affecting the N cycle. We evaluated the rate of N accumulation in soils after livestock removal, with soil data collected at 13 grazed/non-grazed paired sites across the region. Because exclosures were relatively small and surrounded by actively grazed pastures, N accumulation over time was used as a proxy of the minimum N input to the ungrazed areas. Soils of exclosures with deep soils (>30cm depth, n=9) showed, on average, an increase of 43 kg/ha.yr of total N (in 0-30cm depth) relative to the paired grazed sites. Exclosures in shallow soils (<30cm depth, n=4) did not accumulate N in soils, probably because of high N losses by leaching. Legumes were not present in exclosures or in the grazed pairs. No papers measured rates of non-symbiotic N fixation in the region, but for other regions, it has been estimated as 1 to 5kg/ha.yr. Assuming these proportions, our estimates of atmospheric N deposition in this region could be much higher then previously thought (~40 kg/ha.yr vs ~4 kg/ha.yr). Simulations using the CENTURY model reproduced the observed patterns and suggested that higher volatilization from urine and dung patches are accountable for higher N losses in grazed sites. Enriched soil δ15N in grazed sites can result from high rates of N volatilization, due to the fact that the NH3 products are heavily depleted in 15N. However, in exclosures with deep soils, changes in soil δ15N were small and not significant among grazed and ungrazed paired sites. In contrast, in exclosures with shallow soils not accumulating N, δ15N values were significantly depleted in ungrazed (5.5‰) respect to grazed sites (6.6‰). Greater losses of N in the grazed matrix of these rangelands, which extend over more than 40 million hectares in the region, could be increasing the amount of reactive N in the atmosphere (mainly as NH3), and increasing local N redeposition. Ongoing rain collections showed high NH4 inputs in rain. As much as 4.02 mg/l were collected in one rain event in August-2005. Precarious extrapolation of these values to annual deposition gives an annual value of 48.2 Kg/ha.yr. Currently rain collectors are being installed to continue rain measurements. Our work suggests that domestic herbivores are opening the N cycle through increased N emissions and local redeposition of reactive nitrogen.

Agricultural Best Management Practices in Denmark

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Abstract

Indoor air quality and gaseous emissions from livestock facilities have been hot themes in Denmark during the last decade; much research is also in progress for the next decade. The driving forces are the EU directives, Danish rules, and the public concern about the human health and the environment, regarding dust, odour, and ammonia. With fulltime employment in pig and poultry houses, the dust burdens is of big concern for the workers, and comprehensive investigations are carried out in Denmark on methods to reduce the dust concentration in animal houses. The most efficient method today is spraying a small amount of rapeseed oil, controlled by animal activity. Nearby livestock facilities, the outdoor environment is especially disturbed by the odour emission from the facilities. It is well documented that the odour emission can be reduced very much by air scrubbers and bio-filters with good maintenance. The problems are the durability, maintenance requirements and energy consumption. Investigations are in progress in Denmark on how to reduce the odour emission by air scrubbers with low pressure losses. Ammonia emission is another hot theme because approval of new animal facilities and renewed facilities with increased production capacity is depending very much on the documented future ammonia emission, based on emission factors. There are big differences between the emission factors for different housing systems. For dairy cows in cubicle houses with slatted floor and underlying scrapers in the alleys, the emission is e.g. 0.06 kg NH_3-N per kg total N in manure, but 0.10 kg NH_3-N per kg total N for cubicles with solid floors. For layers in cages with manure belts, the emission is 0.10 kg NH_3-N per kg total N, which is very low compared to other types of layer houses. This illustrates that the housing system has a very big impact on the ammonia emission. For a certain system, the management has also a big impact. One of the efficient solutions in Denmark to reduce ammonia emission is to add 0.5% sulphuric acid to the slurry, which reduce the emission by 70%. In respect to reduce ammonia emission from slurry storages, the slurry tanks must in Denmark be covered with e.g. a tent or the slurry surface must be covered with a controlled compact floating layer.

Introduction

The animal production in Denmark has been undergoing drastic changes over the last five decades in respect to herd size, stocking density and housing systems (Pedersen, 2005). As a consequence, the indoor air quality and the emission from animal facilities are also developing fast over time. For instance five decades ago, the average number of growing-finishing pig per farm in Denmark was around 10, and today, 600. The space per growing-finishing pig went down from 1.6 m^2 in the 1950s to 0.7 m^2 in the 1990s and is today again slightly increased to 0.8 m^2, due to EU and Danish regulations. Until the 1950s, no slatted floors were used in Denmark. In the 1970s the use of slatted floors was growing very fast, and in the late 1990s, two thirds of all pens for growing-finishing pigs was with fully slatted floors without bedding. Due to EU and Danish regulations, fully slatted floor will be totally forbidden from 2013, and in the future slatted floor will only be allowed in a third of the pen surface for growing-finishing pigs. Together with another new EU rule, rooting material is obligatory for growing-finishing pigs, why it can be expected that there will be an increase in use of straw as bedding in many pig facilities. Also cooling by water spraying in pig houses in hot periods is today obligatory in Denmark. For cattle and poultry there have also been drastic changes over time. Altogether facilities for animal production are changing fast, and it may be expected that the present state-of-the-art will be out of date already in few years. As a consequence the indoor air quality and the emission will also change.

From a scientific point of view, very few scientists in the 1970s were concerned about the outdoor environment. It was mainly a question on how to improve the indoor climate in respect to improving efficiency of the animal production. The emission of e.g. ammonia emission via ventilation and evaporation of ammonia from storages was of little concern. In some way manure from animal production was considered only as waste product, which could easily be replaced by fertilizers. In the 1980s the concern about the emission was growing and at the same time it was experienced that many pig farmers got problems with their lungs, due to dusty indoor climate. Today there is a very big awareness about the negative impact of ammonia on the environment. A review on ammonia emissions from animal production facilities is also shown by Pedersen et al. (2004), based on a CIGR ammonia conference held in Denmark in 2003. Another increasing problem of more cosmetic nature is the odour burdens for workers in animal facilities and especially for people living in the vicinity of animal facilities. Because odour is mix of many different chemical components in small concentrations, it is a real challenge to examine and get rid of the smell.

This paper deals with the three main air quality factors; dust, ammonia, and odour concentrations and emissions.

Dust

Dust Reduction Methods

In former time airborne dust was not recognized as a problem in Denmark, because the work in pig houses only covered a minor part of a working day. Today, the indoor climate is "improved" by insulation of floors, walls and roofs and better ventilation, but unfortunately the indoor air is much dustier, especially in pig and poultry houses, opposite the more moist cattle buildings. At the same time it is fulltime job to work in pig facilities. The dust problems in pig houses was experienced already in the 1960s, but the real awareness about the negative influence on lung function for stockmen was awakened later, when it was common with bigger herds and fulltime work in pig houses. Today all farmers and stockmen know that if they do not protect themselves, there is a big risk for reduced lung function after years of work in pig houses.

In the EU project PL 900703, it was shown (Takai et al. 1998) that the average dust concentration in cattle houses were 0.38 mg total dust and 0.07 mg respirable dust per m^3 air. The concentration in pig houses averaged 2.19 mg total dust and 0.23 mg respirable dust per m^3 of air, and in poultry houses 3.60 mg total dust and 0.45 mg respirable dust per m^3 air. It shows that the dust concentrations in pig houses are around five times higher than in cattle houses, and that the dust concentration in poultry houses is even higher. The Danish hygienic limits for animal buildings are 3 mg total dust per m^3. Because there is a big variation from one animal house to another, there are many pig and poultry houses where the dust concentration is above the threshold. These results should be considered in relation to the relative humidity, which in cattle buildings in Northern Europe is typical 80% but only about 65% in pig and poultry buildings with more dry feed (Seedorf et al. 1998). The dust burden is in fact a real problem for pig and poultry farmers, because long time exposure can reduce the lung function for humans. The lifetime for farm animals is only up to a few years, why long time exposure will normally not harm the animals, but because gases as e.g. ammonia are bound to the dust, it indirectly can harm the animals.

There are two main strategies to solve the dust problem, namely:

- To wear personal protection as e.g. dust mask or a helmet with fresh air supply
- To reduce the dust burdens in the animal house it self.

From the stockmen point of view the best solution is to reduce the dust burdens, because it is not comfortable to use mask or helmet. It must also be taken into account, that masks may only be used 3 hours per day, because it has a negative effect on breathing.

At RCB, investigation on methods to reduce the dust concentration in pig houses has been carried out since the early 1980s, including vacuum cleaning, Ionization, straw versus no straw, wet versus dry feeding, recirculation of filtrated air, electrostatic filter, fogging with water, fogging with rape seed oil and fat in diet. Also The National Committee for Pig Production has since the 1990s carried out research on dust in pig buildings. Different technical solutions have been carried out at RCB as official test or in research programs. Research at RCB showed in the early 1990s that the dust burden in animal houses is strongly related to the animal activity, why an animal activity sensing system based on PID (Passive Infrared Detector) was developed (Pedersen and Pedersen, 1995). As shown in Figure 1 the dust concentration in animal houses is strongly related to the animal activity.

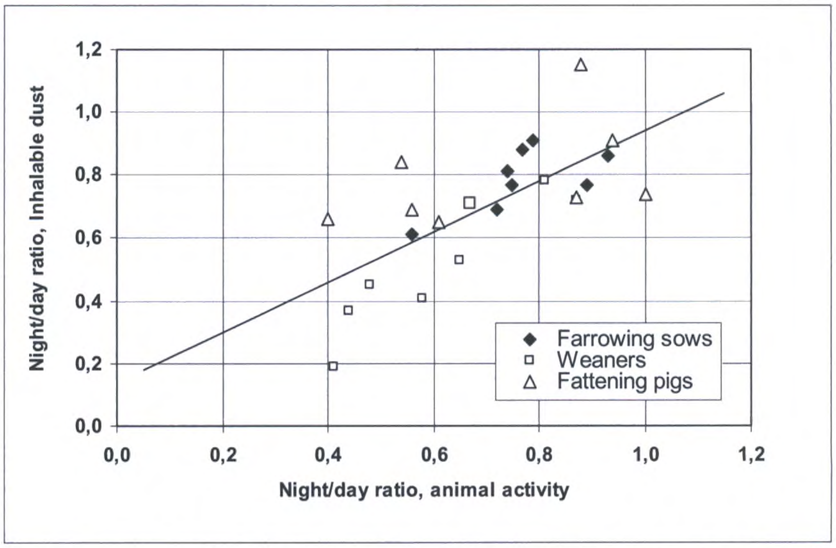

Figure 1. Correlation between animal activity and air borne dust in weaner house

Figure 2 shows another example (Pedersen and Takai, 1999) on how the diurnal variation in the dust concentration in a pig house in depending on the animal activity.

The measurements are carried out with a particle counter and shows good correlation between animal activity and the dust concentration.

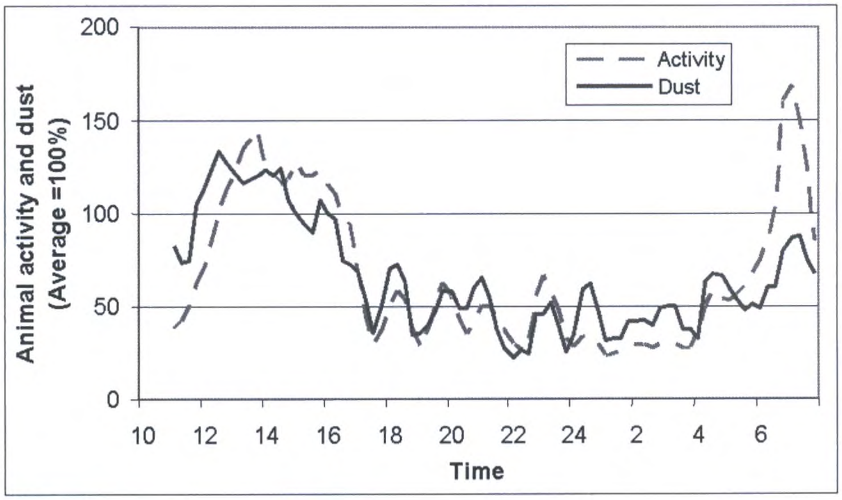

Figure 2. Dust in relation to animal activity in a weaner house

As mentioned above comprehensive work on how to reduce the dust burdens was initiated at RCB in the 1980s, and the possibility of abating the dust with spraying small amounts of oil in the animal house was tested. Many different techniques and types of oil were tested, and finally rape seed oil was selected, because it is an inexpensive vegetable oil. The results were promising already from the start. Figure 3 shows the high-pressure spraying of rape seed oil in growing-finishing house.

Figure 3. Example of spraying of rape seed oil

To improve the system further, an experiment was carried out with rape seed spraying, controlled by animal activity.

Figure 4 summarizes the different methods tested at RCB, and it shows that reductions of up to 88% are obtained by spraying rape seed oil, controlled by animal activity, in such a way that spraying is only done when the animal activity is above the threshold. (Takai and Pedersen, 2000)

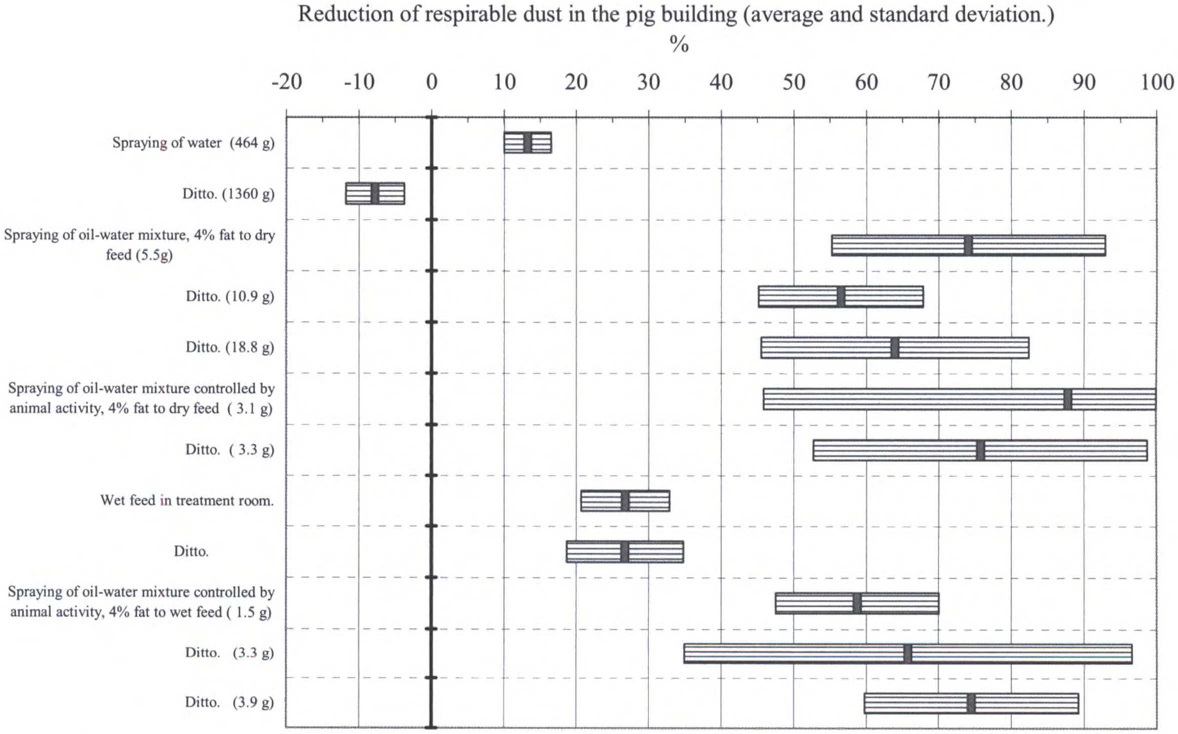

Figure 4. Reduction of respirable dust in pig buildings, from FCB tests (Rape-seed/water in g per day per pig)

Ammonia

Over the last four decades, ammonia measurements have often been a part of air quality investigations in animal houses in Denmark, because it has been one of the important parameters about indoor air quality in respect to animal health. In the 1970s with pig pens with partly slatted floor, bedding and around 1 m^2 pen area per pig, the average ammonia concentration was 5 ppm ammonia. In the 1990s Denmark was part of a comprehensive EU measuring program in Germany, the Netherlands, England, and Denmark, carried out in enclosed cattle, pigs, and poultry houses. In Table 1 shows the concentrations of ammonia measured in Danish houses in average of 10 houses in each group (Groot Kooerkamp et al. 1998)

Table 1. Ammonia concentrations and emissions measured in Denmark in the 1990s

	Ammonia concentration (ppm)		Ammonia emission (mg/h)	
	Average	Maximum	Per animal	Per HPU**)
Dairy cows, litter	2.7	18.6	560	485
Dairy cows cubicles	3.3	20.1	987	848
Beef cattle, slats	6.4	17.7	580	1166
Calves, litter	1.9	5.7	332	1024
Sows, slats	8.7	22.1	730	1234
Weaners, slats	5.3	17.9	46	750
Growing-finishing pigs, litter	9.1	21.7	394	2241
Growing-finishing pigs, slats	14.9	43.4	319	1635
Laying hens, deep litter	25.2	72.3	38.3	3643
Laying hens cages	6.1	14.5	7.7	711
Broilers, litter *)	8.0	40.3	8.9	343

*) Average of four measurements over a production circle

**) One HPU (Heat Producing Unit) is corresponding to 1000W in total heat production at 20°C

The investigation shows that in houses for finishers, the ammonia concentration in the 1990s is about 70% higher as found in the 1970s. It also shows that the ammonia concentration is much bigger in houses with slatted floor as in straw bedded pens. Since the 1990s new facilities with proper housing design and management often shows much lower ammonia concentrations.

For layers, the ammonia concentration and emission is very high for laying hens in deep litter.

Today almost all new building facilities for dairy cows are with cubicles and natural ventilation. It is open houses with very high air exchanges, and it is a real challenge to measure the ammonia emission from such facilities. Due to very big ventilation openings, which can be extended to an open sided building, it is necessary to measure the ventilation flow indirectly by tracer gases or by means of the increase in carbon dioxide concentration due to an animal CO_2 production of about 0.185 m^3 per HPU per hour. Figure 5 shows the results from a Danish investigation based on carbon dioxide measurements (Zhang et al. 2005).

The ammonia emission, which is the product of the ammonia concentration and the ventilation flow, is strongly dependent on the indoor temperature and increases roughly proportional with the indoor temperature. In this example with naturally ventilated houses, the ventilation openings are normally fixed, why the ventilation rate can be considered as nearly independent of the indoor temperature. In houses with mechanical ventilation with temperature dependent ventilation rate, the relation between indoor temperature and ammonia emission will be different.

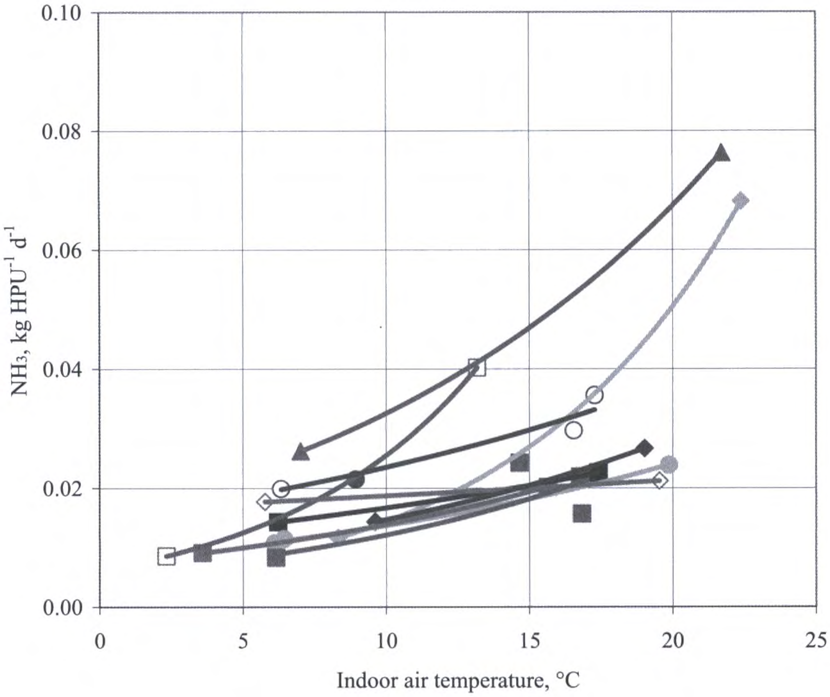

Figure 5. Average NH_3 emission rates for nine buildings with different slurry handling principles over the measurement period

Also the storages are contributing to the ammonia emission from animal facilities. In Denmark slurry tanks must be covered by a natural floating-layer of manure or be covered e.g. by a tent as shown in Figure 6. By use of a tent, the ammonia emission can be reduced to few percents.

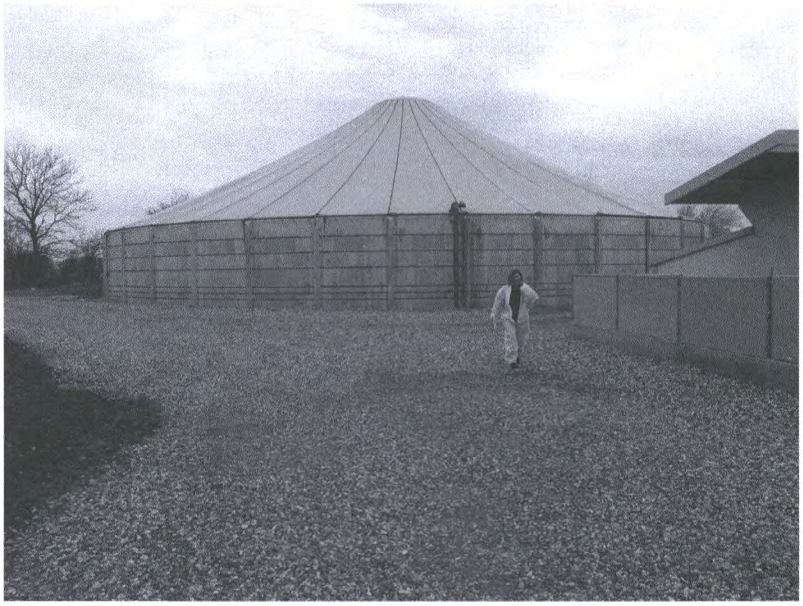

Figure 6. Slurry tank with tent for limiting the ammonia emission from storages

In Denmark the ammonia emission from animal facilities is strongly regulated by authorities, based on the knowledge of nitrogen release from the animals and evaporation factors. The nitrogen release is shown in Table 2, where N is total N including both ammonium N and organic N (Ministry of environment, 2003). The guidelines are under revision and attempted to be finished in 2006.

Table 2. Danish norm values for nitrogen release per animal

Specie	**Type**	**Kg N in faeces + urine per animal per year**
Pigs	Sows	26.72
	Weaners	0.65
	Growing-finishing pigs	3.14
	From weaning to slaughtering	3.79
Cattle (large races)	Dairy cows	127.3
	Calves, 0-6 months	5.8
	Heifers, 6 months to calving	30.8
	Bulls calves, 6 months to 382 days	24.3
	Cows with suckling calves	73.3
Mink	Female yearly with puppies	4.59
	Per produced fur	0.88
Poultry	Broilers, 35 days	0.0405
	Broilers, 40 days	0.0536
	Broilers, 45 days	0.0665
	Eco-broilers, 81 days	0,127
	Layers, cages	0,655
	Layers, floor keeping	0,857
	Layers with outdoor access	0,800
	Layers, ecological	0,879
	Brooding hens	0.907
	Turkeys, hens	0,481
	Turkeys, cocks	0,878
	Ducks	0,173
	Geese	0,561

For each type of animal and housing system, the Danish norm prescribes standard values for how much of the nitrogen, released from the housing system by faeces and urine, there is evaporated. Table 3 shows some of the evaporation factors. The table shows that there are big differences between the emission factors for different housing systems. For dairy cows in cubicle houses with slatted floor and underlying scrapers in the alleys, the emission is e.g. 0.06 kg NH_3-N per kg total N in manure, but 0.10 kg NH_3-N per kg total N for cubicles with solid floors. For layers in cages with manure belts, the emission is 0.10 kg NH_3-N per kg total ammonium, which is very low compared to other types of layer houses with floor keeping. This illustrates that the housing system has a very big impact on the ammonia emission. For a certain system, the management has also a big impact

Table 3. Emission factors from Danish animal housing facilities (per cent of excreted N in faeces and urine)

		Solid floor	**Partly slatted floor**	**Fully slatted**
Cattle	Dairy cows, tie stall, dung channel	5	3	
	Dairy cows, cubicles	10	6-8	
	Dairy cattle, deep litter	6-7		
Pigs	Pregnant sows	16	10	14
	Growing-finishing pigs	18	12	16
	Weaners,	25	10	16
	Farrowing sows,		10	20
Poultry	Broilers, traditional	20		
	Broilers, ecological	25		
	Layers, floor keeping, with outdoor access	30		
	Layers, cages, manure cellar	12		
	Layers, cages, manure conveyer	10		
	Layers, eggs for brooding	30		
	Turkeys, ducks, geese	20		

The ammonia emission can finally be calculated by multiplication of Kg N (faeces + urine per) animal per year in Table 2 with the evaporation factors in Table 3.

Many other factors impact on the ammonia emission as e.g. the feed composition in respect to the protein content.

In Danish investigations not published, it is indicated that the ammonia emission from growing-finishing pigs is about 25% lower for pigs using maize silage as rooting material than for pigs using straw. Another interesting result from the same experiments shows that the methane emission increases by about 80% using maize silage as rooting material compared to the use of straw.

Mink Facilities

Housing facilities for mink are based on elevated cages, where the feces and urine drop from the cage bottom to the underlying slurry gutter, often in two-row open mink houses. Together with protein rich feed, it gives a high potential for ammonia emission. To show the influence of management and temperature on the emission, experiments were carried out in a two row open mink house as shown in Figure 8 (Pedersen and Sandbøl, 2002). The results show that the ammonia emission is very sensitive to both the surrounding temperature and the frequency of cleaning the slurry gutter.

BAT- Best Available Technique

In Europe, many countries have developed an evaluation system for evaporation of ammonia and greenhouse gases from different production systems under the umbrella BAT. The idea is to guide farmers to select environment friendly production systems. The BAT notes are also used by regional governments in giving permissions to changes and enlargements of existing animal production systems and to establishment of new farms. In Table 4 is shown some examples of Danish BAT notes:

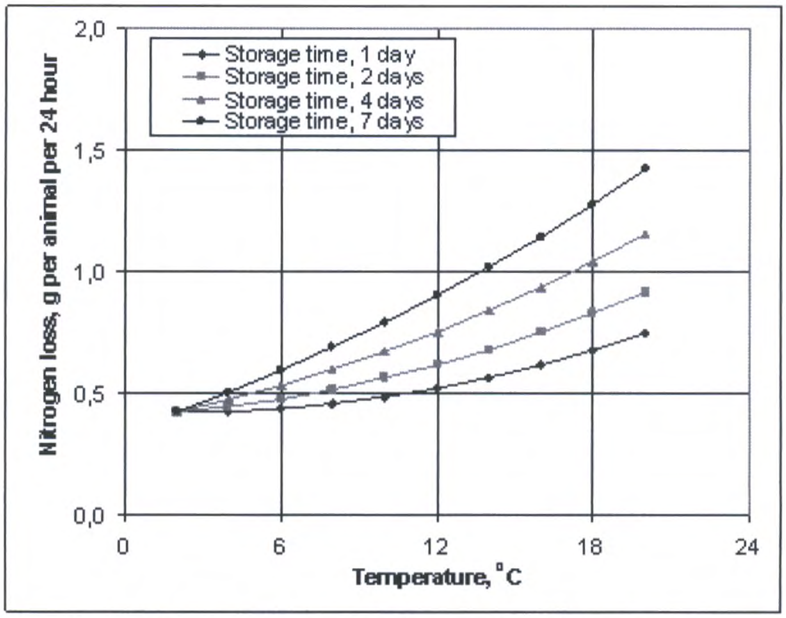

Figure 8. Nitrogen losses from two-row open house for mink of 1800 g

Table 4. Danish BAT notes on ammonia emission

Type and group number	Principles	Reference house	Reduction, %		
			Dust	Ammonia	Odour
Layers 105.02-51	Pit drying of manure, floor keeping deep litter and scraping area	Floor keeping, 2/3 deep litter, 1/3 manure cellar	-	50-60	-
Layers 105.02-52	Manure drying in layer houses, cages	Manure cellar	-	50-70	-
Pregnant sows 106.01-51	Cooling of bottom in manure cellar	Partly slatted floor	-	30	-
Farrowing sows 106.02-51	Farrowing pens with partly slatted floor	Fully slatted floor	-	50	-
Weaners 106.03-52	Two-climate pens, partly slatted floor	Fully slatted floor	-	30	-
Growing-finish. pigs 106.04-52	Partly (1/3) slatted floor	Fully slatted floor	-	15	-
Growing-finish. pigs 106.04-53	Cooling of bottom of slurry channel, partly slatted floor.	Fully slatted floor	-	30	-
Growing-finish. pigs 106.04-58	Fully slatted floor	Air washing with sulphuric acid cleaning of up to 60% of exhaust air	-	50	Small reduction
Dairy cattle 107.04-51	Pre-manufactured floors with urine grooves and drains	Cubicles and slatted floor above ring shaped manure channel with daily circulation	-	50	-

In addition to Table 4, there is a list of BAT candidates, not yet confirmed. Some of them regard reduction of the pH in slurry channels, by means of adding 0.5% sulphuric acid to the slurry and circulating it by a special technique. The reduction of ammonia emission is about 70%, which is very good, but the economy and other aspects have to be considered further.

Odour Emission

Much research is carried out worldwide over the last decades on climatization of animal houses, and many examples are shown on how to improve indoor climate and to reduce the emission from animal houses. Why are those strategies and technical solutions not implemented in praxis? The answer is simple: because it is primarily a question about economy. In the 1970s some few Dutch farmers with their farms in villages installed air scrubbers in combination to existing exhaust fans in pig houses. Visits on sites convinced the author that the odour was reduced very much, and the remaining odour was turned to a mouldy smell. Also measurements carried out by SBI (Danish Building Research Institute) and by DLU (The Agricultural Experimental Center, Ørritslevgaard) in the 1970s, showed by olfactorimetric that it was possible to reduce the odour very much. In the last three decades many experiments are carried out worldwide on air scrubbers and bio-filters, and today it is well proved that it is possible to reduce the odour. Due to increasing production cost for electricity, maintenance and manpower, very few odour reduction plants are taken into use. The coming years of research on bio-scrubbers and bio-filters will probably give a better understanding of the mechanisms which control the efficiency of such systems.

Many other examples of odour reduction are tried. For instance, feeding the animal with small amounts of plant products, mixing the slurry with clay minerals, etc., but sustainable solutions are not yet seen.

Measurements on odour emission in ongoing at more research units in Denmark. Some recent results carried out at Danish Agricultural Advisory Service, are shown in Table 5

Table 5. Odour measurements in cattle and poultry houses

		Odour production	
		Per animal (OU/s)	Per 1000 kg (OU/s)
Cattle	Dairy cows, tie- and loose housing	145	242
Poultry	Hens in cages	0.75	398
	Hens in floor keeping	1.68	897
	Broilers	1.77	1217

The odour emission from broilers seems very high compared to cattle, expressed per 1000 kg body mass, but the manure production of 1000 kg broiler is much higher than from 1000 kg dairy cows. Expressed in another way, the total heat production, related to the metabolic mass of animals, broiler produces about eight times as much heat as 1000 kg dairy cow, which must be taken in consideration when evaluating the data.

A big task for the future will be to learn more about the components include in the odour from animal houses and to get a better understanding of the behavior of the different chemical components in respect to half-time reduction, etc. In Table 6 is shown the results of a Danish experiment, where the results of an odour panel are compared to results from a chromatography method. The ranking is based on the number of panel members who detected the individual odorants. (Kai & Schäfer, 2004). The percentage is referring to how many out of seven panelists were able to identify some smell. The table just illustrates a step in the right direction of a long path leading to sufficient understanding of odour emission from animal production facilities.

Table 6. GC- Olfactometry analysis versus odor panel description

Pct.	GC-Olfactometry analysis Odor panel description	GC-MS analysis Odor compound
100	Sweat, sour, pig house, cheese	Butanoic acid
100	Pig odour, forest floor	Not identified
100	Sour, pig house, feet	Not identified
100	Flower, fresh, fermented, sour	Not identified
86	Pig house, faecal	4-methyl-phenol
86	Forest floor	Not identified
86	Faecal, pig house, unpleasant	Not identified
71	Sour	2-methyl-propionic acid
71		Not identified
71	Mushroom	Not identified
71	Boiled rice	Not identified
71		Not identified
71	Sour, unpleasant, cheese	Not identified
71	Tar	Not identified
71	Faecal	Not identified
71	Pig house	Indole
57	Pig house	Octanoic acid
57		Not identified
57		Not identified
43		Propanoic acid
43		Phenol
43	Feet	Not identified
43	Burnt, tar	Not identified
43	Tar	Not identified
43		Not identified

Conclusion

The challenge for the next decades will be:

- To improve the indoor climate in respect to humans and animals and minimizing of emission of dust, gases and odour from animal facilities;
- To develop efficient inexpensive air cleaners for exhaust air, with low investment, running costs and need maintenance;
- To meet the continuous fast changes in animal housing systems with appropriate solutions

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Scaling: Field Experiments and Measurements

Observing Air Quality from Space: From Research to Decision Support

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Abstract

Air pollution is a major cause of respiratory and cardiovascular disease. The principal pollutants of concern are ozone and aerosols, which are produced in the atmosphere by chemical reactions involving nitrogen oxides ($NO_x = NO + NO_2$), volatile organic compounds (VOCs), carbon monoxide (CO), and sulfur dioxide (SO_2). These precursors have both anthropogenic (principally combustion) and natural sources. Aerosols are also directly emitted to the atmosphere by combustion, dust suspension, and sea spray.

High concentrations of ozone and aerosols originating from human industrial and agricultural activity are a threat to public health in most densely populated regions of the world. Surface air measurement networks have insufficient coverage to monitor population exposure, and are generally lacking in the developing world. Ozone and aerosol formation depend in complex and nonlinear ways on the concentrations of precursors, for which little in situ observational data are available. Management decisions for air quality require emission inventories for the precursors, and these are generally constructed by a "bottom-up" approach involving application of emission factors to activity rates. Such inventories are often uncertain by a factor of 2 or more, particularly in the developing world. Air quality management also requires better understanding of the long-range transport of pollution, including on intercontinental scales.

Recent advances in tropospheric remote sensing have stimulated research interest in the application of satellite observations to air quality issues. Observations of NO_2 and formaldehyde from a variety of space-borne instruments have been used to place new top-down constraints on sources of NO_x and VOCs and their interannual variability and trends. Observations of CO from satellite missions have also been used to constrain CO sources and to track the intercontinental transport of pollution plumes. Combined observations of ozone and CO from the NASA Aura Mission are offering constraints on intercontinental transport of ozone pollution. Aerosol optical depth (AOD) observations from the other NASA Earth Observing System satellites have been used to infer surface air concentrations of PM, providing new insights in particular in the developing world where few in situ data are available. Assimilation of these measurements of AOD observations, and those of trace gas abundances as well, are being used in near-real-time air quality analyses and forecasts.

These research advances have come under notice by the air quality management community, which is increasingly seeing satellite observations as a crucial part of a hierarchy of observations and models needed for future air quality management, both for monitoring and for improving understanding of source-receptor relationships and of the underlying processes. This paper will review how satellite assets already in space are being exploited for characterizing, understanding and predicting air quality, and the limitations of these current missions for which air quality applications were in many cases incidental to the original mission goals. The paper will also present some of the considerations for developing a strategy for future space missions with increased capability for air quality applications. Some of the key considerations in the design of new instruments are the spatial and temporal resolution required to effectively monitor air quality from space, which in turn informs the consideration of the various potential orbital vantage points. An approach that has been used to address the issue of spatial resolution by calculating the spatial length scales of trace gases within the boundary layer and free troposphere using both in-situ aircraft data from five different NASA aircraft campaigns and simulations with an air quality model will be presented.

Measurement and Analysis of Ammonia and Hydrogen Sulfide Emissions from an Anaerobic Swine Waste Treatment Lagoon and Confinement Building in North Carolina

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Abstract

Emissions of atmospheric ammonia-nitrogen (NH_3-N, where NH_3-N = (14/17)NH_3) and hydrogen sulfide (H_2S) from a commercial anaerobic swine waste treatment lagoon and a fan-ventilated swine confinement building located next to the lagoon were measured over a one year period. Continuous simultaneous measurements were made at the lagoon using a dynamic flow-through chamber system for ~1 week during four seasons in an effort to examine diurnal and seasonal variability and the respective relationships of NH_3-N and H_2S emissions to lagoon physiochemical properties. During the fall and spring, average NH_3-N fluxes were 1634 ± 505 and 2495 ± 465 $\mu g\ N\ m^{-2}\ min^{-1}$, respectively. The lowest fluxes were observed during the winter where average flux values were 1290 ± 246 $\mu g\ N\ m^{-2}\ min^{-1}$. The lowest fluxes for H_2S were also observed during the winter season, ~0.0 $\mu g\ m^{-2}\ min^{-1}$. Average fluxes increased slightly during the fall (0.3 ± 0.1 $\mu g\ m^{-2}\ min^{-1}$) and spring (0.5 ± 1.0 $\mu g\ m^{-2}\ min^{-1}$) and were observed at highest flux values during the summer (5.3 ± 3.2 $\mu g\ m^{-2}\ min^{-1}$). Generally, the lagoon emissions for H_2S were ~3-4 orders of magnitude less than NH_3-N.

Continuous simultaneous NH_3-N and H_2S emissions from a swine confinement house were also made for ~1 week period during four seasons. Normalized NH_3-N emission rates were highest in winter (33.5 ± 22.1 g N day^{-1} 500kg live animal $weight^{-1}$ (LAW)) and lowest during fall (11.6 ± 7.2 g N day^{-1} 500kg LAW^{-1}). Normalized H_2S emissions were lowest in summer and fall (1.4 ± 0.7 and 1.7 ± 0.5 g day^{-1} 500kg LAW^{-1}) and were highest during the winter and spring seasons (4.2 ± 2.2 and 4.3 ± 1.0 g day^{-1} 500kg LAW^{-1}).

Introduction

Changes in livestock production methods in the U.S. are in turn changing emissions of trace gases (e.g., sulfur and nitrogen species) into the atmosphere (Aneja et al, 2006). In North Carolina, for example, large-scale commercial operations have emerged over the last few years, dramatically increasing the number of hogs in a geographically concentrated area. In this state, there are currently over 1400 operations with more than 1000 head, accounting for almost 99% of the state inventory (http://www.nass.usda.gov/QuickStats/). Subsequently, emissions of potentially harmful gases such as ammonia, (NH_3) and hydrogen sulfide (H_2S) from confined animal feeding operations (CAFOs) have become a major problem in recent years. Public concerns about potential environmental and health effects of air emissions from CAFOs have increased in parallel with the growth and consolidation of this industry.

Ammonia released from near-surface sources (i.e. waste treatment lagoons, confinement houses) into the atmosphere has a relatively short lifetime of ~1-5 days (Warneck, 2000) and may deposit near the source through dry or wet deposition. However, ammonia can also participate in atmospheric reactions (e.g. gas-to-particle conversion) once airborne, forming ammonium aerosols such as ammonium sulfate, -nitrate, -chloride, which tend to have longer atmospheric residence lifetimes (~1-15 days) owing to a decrease in dry deposition velocity (Aneja et al., 1998) and therefore may be transported and deposited further downwind from the source. An environmental hazard in eastern North Carolina associated with gaseous ammonia and ammonium aerosols is deposition into sensitive coastal river systems where nitrogen loading may lead to enhanced eutrophication and soil acidification, which may in turn upset plant nutrient balances near sources (Paerl, 1997).

Hydrogen sulfide is a colorless, potentially lethal gas released from swine manure (U.S.EPA, 2001). It is produced as manure decomposes anaerobically, resulting from the mineralization of organic sulfur compounds as well as the reduction of oxidized inorganic sulfur compounds such as sulfate by sulfur-reducing bacteria (U.S. EPA, 2001). The U.S. Center for Disease Control (CDC) warns that brief exposures to high concentrations (> 500 ppm) can cause unconsciousness or death (ATSDR, 2004). With a low odor threshold ranging from 0.0005 to 0.3 ppm (ATSDR, 2004), it is also one of the primary gases released from swine facilities that is associated with odor complaints due to it's characteristic "rotten egg" smell. Donham et al. (1982) reported that hydrogen sulfide appeared to be the main toxic substance in liquid manure associated with death and illness for people with acute exposure to gases emanating from liquid manure. Campagna et al. (2004) have reported a correlation between elevated ambient H_2S concentrations and hospital visits for respiratory diseases .Potential negative health effects of overall emissions from hog farms have been identified in production workers and neighboring residents that include respiratory illnesses such as bronchitis and asthma, and increased psychological stress (Schiffman, 1998). However, it is noted that H_2S is just one component of many odorous and potentially harmful gases that have been identified in hog farm emissions.

Significant efforts have been devoted to understanding emissions of ammonia from waste storage treatment lagoons (Harper et al., 2000; Aneja et al., 2000, 2001a, b). Arogo et al. (2003) have reviewed measurement techniques and studies undertaken to estimate NH_3 emissions from both swine lagoons and animal confinement houses. Emissions of ammonia (Zhu et al., 2000; Heber et al., 1997, 2000; Wood et al., 2001, Schmidt et al., 2002) and hydrogen sulfide (Heber et al., 1997; Zhu et al., 2000; Ni et al., 2002; Schmidt et al., 2002) from swine confinement houses have been estimated. To date, few studies have reported H_2S emissions from waste storage treatment lagoons (Zahn et al., 2001; Lim et al., 2003), none from farms in the southeastern U.S. Various factors, such as farming activities (i.e., feed composition, animal density) and regional climates, may affect the emissions of gases into the atmosphere. Emissions estimates generated for one set of conditions or for one type of CAFO may not translate readily to others. It is therefore important for comprehensive emissions measurements to be made from different types of operations.

The primary objective of this research initiative was to investigate and evaluate the variability of ammonia and hydrogen sulfide emissions with respect to diurnal and seasonal variations as well as the influence of meteorological and physico-chemical factors. Data presented here was collected continuously for about a one-week period from an anaerobic swine lagoon and about one week from a swine finishing barn during each season (i.e., fall, winter, spring, summer) for one year at a commercial hog farm in eastern North Carolina. Generally, the barn measurements were made immediately prior to following the lagoon experimental, except during the fall season where lagoon measurements were made in fall 2004 and barn measurements were made in fall 2005.

Methods and Materials

Physiographic Location and Farm Description

The experimental site is a commercial swine finishing farm, operating under steady-state conditions, located in Jones County in the southeastern Piedmont region of the state. The on-site waste storage treatment lagoon is 3.06 Ha (30,630 m^2) and the farm maintains eight fan-ventilated confinement houses with ~800-900 animals housed in each barn. Each barn has a shallow manure collection pit which is emptied once a week. The farm utilizes a conventional "lagoon and spray" technology as its primary means of handling effluent. Effluent is flushed directly from the hog barns into the storage lagoon where it is treated via natural microbial processes. The stored wastewater is used to recharge the barn pits, and also periodically irrigated over on-site agricultural crops for nutrient enrichment purposes.

Dynamic Flow-Through Chamber System

A flow-through dynamic chamber system with a variable-speed motor-driven continuous impeller stirrer (Kaplan et al., 1988; Kim et al., 1994; Chauhan, 1999; Aneja et al., 2000) was employed to determine NH_3-

N and H_2S flux from the lagoon. The translucent plastic cylindrical chamber, 0.25 m internal diameter, 0.46 m internal height of chamber above water or soil, and volume $0.025m^3$, is fitted into a circular hole cut into the center of a 0.61 x 0.61 m floating ½" thick ultra-high molecular weight (UHMW) polyethylene platform. The chamber penetrated into the lagoon ~7 cm, creating an internally closed system. The platform is supported by 0.15 m diameter by 1.68 m length PBC piping for floatation, designed to sit a few centimeters above the lagoon in order to minimize experimental effects and simulate atmospheric conditions at the lagoon surface as accurately as possible. A schematic of the chamber system is shown in Figure 1.

The chamber was lined internally with a 2 mil fluorinated ethylene propylene (FEP) Teflon sheet to reduce chemical reactions and build up of temperature inside the chamber. Compressed zero-grade air was used as a carrier gas and pumped through the chamber at a variable flow rate of ~0.009-0.012 m^3 min^{-1} utilizing a Model 810-S Mass Trak Flow Controller (Sierra Instruments, Monterey, CA). The in-flowing air was carried through a ¼" o.d., 5/32" i.d Teflon FEP sample line to the chamber. The air inside the chamber is ideally well-mixed by a variable-speed motor-driven Teflon impeller stirrer ranging from speeds of 40-60 rpm for this study.

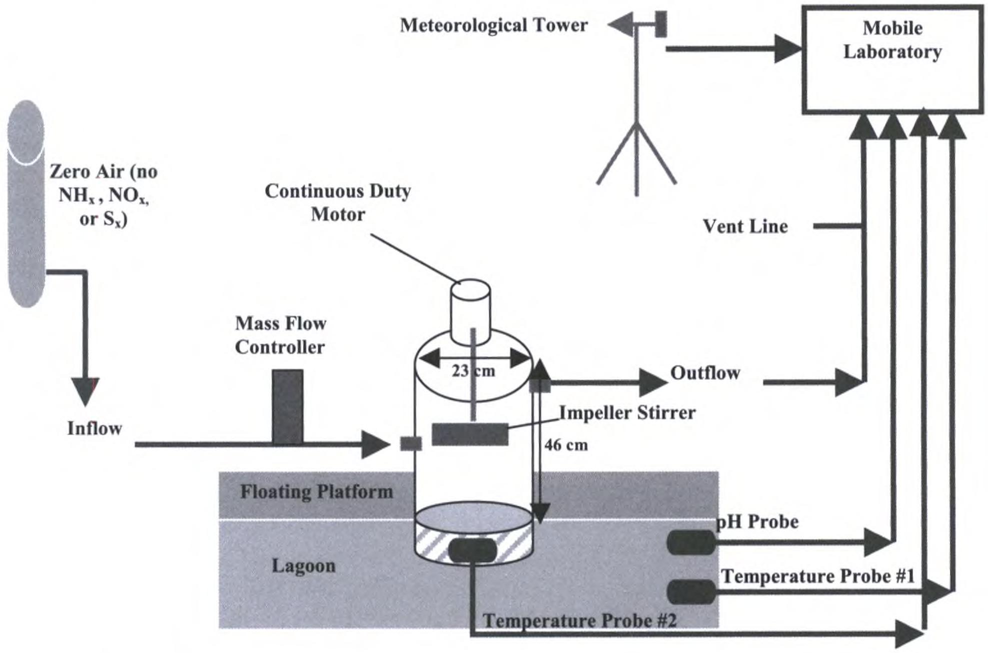

Figure 1. Schematic of dynamic flow-through chamber system configured to measure emissions from a swine waste treatment lagoon

A vent line was fitted to the exiting sample line to prevent pressurization and was periodically bubble tested to check for under pressurization and/or leaks in the enclosed system. The entire closed system was lined with Teflon inside the chamber and stainless steel fittings in order to minimize chemical reactions with sample flow. The sample exiting the chamber travels through the sample line and is then split in order to deliver the sample simultaneously to the different gas analysis instruments.

Lagoon Flux Calculation

In order to calculate NH_3-N and H_2S fluxes for this research experiment, the following mass balance equation was used for the dynamic flow-through chamber system:

$$\frac{dC}{dt} = \left(\frac{q[C_{air}]}{V} + \frac{JA}{V}\right) - (C)\left(\frac{LA_w}{V} + \frac{q}{V}\right) - R \qquad (1)$$

where C gas concentration inside the chamber

C_{air}	concentration in carrier air
q	flow rate of compressed air through the chamber
V	volume of the chamber
A	surface area of the lagoon covered by the chamber
A_w	inner surface area of the chamber of inner and upper wall surfaces
L	total loss of gas in the chamber per unit area due to reaction with inner and upper walls of the chamber
h	internal height of the chamber
J	emission flux per unit area
R	gas phase reactions inside the chamber

Since zero-grade air was used as the carrier gas, C_{air} was assumed to equal zero and gas phase reactions, R, was also assumed to be zero. Since the air inside the chamber was assumed to be well mixed by the impeller stirrer, C was assumed to be constant within the chamber. At steady-state conditions, the change of concentration with respect to time $\left(\frac{dC}{dt}\right)$ was zero. Therefore equation (10) can be simplified as:

$$\frac{J}{h} = C_{eq}\left(\frac{LA_w}{V} + \frac{q}{V}\right) \tag{2}$$

Loss term, L, is determined experimentally while equilibrium-state gaseous concentration (C_{eq}), flow rate (q), and chamber dimensions (V and h) are all measured. Kaplan *et al.* (1988) has devised a method for calculating loss term by calculating the slope of the plot of $-\ln\left[\frac{C_{eq} - C(t)}{C_{eq} - C_o}\right]$ versus time (t). For this experiment, C_o is the initial equilibrium state gas concentration measured by the chamber system at a constant flow rate ($m^3\ min^{-1}$). C_{eq} is the measured gas concentration at a second equilibrium state at an increased or reduced flow rate into the chamber system. C(t) depicts gas concentration at any time, t, during the transition between the first and second equilibrium states. L is determined by:

$$L = \left(slope - \frac{q}{V}\right)\left(\frac{V}{A_w}\right) \tag{3}$$

Lagoon Sample Collection

Lagoon samples were collected daily during each initiative using sterile plastic 500 mL bottles and submitted to the North Carolina Division of Water Quality (NC DWQ) for total ammoniacal nitrogen (TAN), total Klejdahl nitrogen (TKN), and total sulfide analysis. Lagoon samples collected for TAN and TKN analyses were preserved with sulfuric acid to pH < 2 and samples collected for sulfide analyses were preserved with 6N sodium hydroxide and 2N zinc acetate to pH > 9, according to NC DWQ specifications. All samples were immediately stored on ice (<4°C) and brought to the NC DWQ laboratory within 48 hours for analysis.

Barn Emission Experimental Design

Five ventilation fans, two 92 cm (36”) diameter direct driven and three 122 cm (48”) diameter belt-driven, were located at the west end of the building. The fans were staged to operate as temperature increased inside the building. In order to accurately determine fan flow rates, a Mabuchi VDC motor (Santa Clara, CA) was either (1) mounted to a stainless-steel plate configured to fit over the front of the 92 cm fans or (2) attached to a cylinder sleeve which fit over the fan shaft of the 122 cm fans. Single analog output wires were connected from each motor to a Campbell Scientific CR10X data logger which continuously recorded the measured voltage output. Prior to the experiment, each motor was calibrated in the laboratory to obtain voltage outputs at a specific rpm. The rpm for each fan, as well as “on/off” times, could then be determined and flow rates subsequently calculated. According to manufacturer specifications the direct drive motor on the 92 cm fans is rated at 850 rpm and the 122 cm belt-driven fans are rated at 1725 rpm. However, fan belts may become loose over time and the rpms decrease, thus affecting the flow rate (Janni et al., 2005). Static pressure inside the building was monitored using a Model PX655 Omega pressure transducer.

Taking into account static pressure, the flow rates for each fan size were calculated using the following calculation:

$$CalculatedFlowRate = \left(\frac{ManufacturerFanFlowRate}{SpecifiedRPMs}\right)(MeasuredRPMs) \qquad (5)$$

Due to the nature of the airflow through the building, it is assumed that the gaseous concentrations are uniformly distributed at each fan outlet. A ¼" o.d., 5/32" i.d. Teflon® sample line was inserted inside the chimney of the first 92 cm fan to turn on, between the shutter and fan blade, at roughly half the fan radial distance. The air is drawn into the lines via vacuum pumps from each gas analyzer and the sample line is split in order to deliver the sample simultaneously to the different analysis instruments.

Barn Flux Calculation

It is assumed that the concentration is uniform across the barn at the fans. Therefore, the emission rate is calculated by

$$J = C_g * \sum F \qquad (6)$$

where

where	J	gas emission rate from swine barn
	C_g	gas concentration at fan exhaust
	F	flow rate of each fan

Gas Analyzers and Meteorological Instrumentation

A Model 450C pulsed fluorescence H_2S/SO_2 analyzer and a Model 17C chemiluminescence NH_3 analyzer (Thermo Environmental Corporation, Mountain View, CA) were used to measure the concentration of ammonia and hydrogen sulfide, respectively. Multi-point calibrations (80, 60, 40, and 20% of full-range scale) for the Model 450C and Model 17C analyzers were conducted in the laboratory prior to each sampling campaign. During the field study, zero and span checks for H_2S and NH_3-N concentration were conducted daily.

A 10 meter meteorological tower was erected to measure ambient wind speed and direction, air temperature, relative humidity, and solar radiation. Wind speed and direction were measured at 10 m above the surface and air temperature, relative humidity, and solar radiation measurements were made at 2 m height.

At the lagoon, a Model CSIM11 pH probe (Campbell Scientific Inc., Logan, UT) was used to continuously monitor near-surface (6-7 cm depth) lagoon pH. Two CS107 (Campbell Scientific Inc., Logan, UT) temperature probes simultaneously measured the near-surface lagoon temperatures inside the chamber as well as 0.3 m outside the chamber to ensure there are no significant differences. To measure barn exhaust temperature, a CS107 temperature probe was placed in front of a 91 cm outlet fan.

A Model CR10X data logger equipped with a Model AM 16/32 Channel Relay Multiplexer (Campbell Scientific, Inc., Logan, UT) was used to collect all meteorological, lagoon, and static pressure data and a Model CR23X was used to acquire all gaseous and mass flow data. Data was collected every second, and averaged and recorded over a 15 minute timeframe. The data loggers and gas analyzers were housed inside a temperature-controlled mobile laboratory (N.C. State University Air Quality Ford Aerostar Mini-Van), maintained at ~21°C (~70°F).

Results

Lagoon Flux

The NH_3 and H_2S analyzers were programmed to collect data at 20,000 (maximum concentration range) and 1,000 ppb, respectively. Table 1 summarizes the NH_3-N and H_2S fluxes from the lagoon for each season as well as lagoon temperature and pH, both of which are expected to have a significant effect on emission rates (Aneja et al., 2000; Zahn et al., 2002). The lowest average daily fluxes for both NH_3-N and

H_2S were observed during the winter experimental period, 1290 μg-N m^{-2} min^{-1} and ~0.0 μg m^{-2} min^{-1}, respectively. During the winter season, only 2.3% of the H_2S concentration values were above the minimum detectable limit (1 ppb) for the analyzer and so the flux value was considered to be negligible. The highest observed average daily H_2S flux values, 5.3 μg m^{-2} min^{-1}, were observed during the summer. Generally, almost 87% of the total H_2S flux was observed during the summer season.

Table 1. Statistical summary table of average daily NH_3-N and H_2S lagoon fluxes, lagoon temperature, and pH for each season

Season	Sample Dates	NH_3-N Flux[a,b]	H_2S Flux[b]	Lagoon Temperature[c]	Lagoon pH
Fall	Oct 26 – Nov 1, 2004	1634(505)[d] 1110-3305[e]	0.3(0.1) 0.0-0.8	18.2(1.7) 15.7-23.3	8.09(0.03) 8.02-8.15
Winter	Feb 15-21, 2005	1290(246) 867-2027	~0.0(0.2 0.0-1.2	11.5(1.4) 9.1-14.5	8.12(0.03) 8.02-8.20
Spring	Apr 14-19, 2005	2495(465) 1565-3216	0.5(1.0) 0.1-7.1	15.1(1.7) 12.4-19.8	8.10(0.02) 8.03-8.15
Summer	Jun 14-18, 2005	4294[f] 3864-?	5.3(3.2) 0.8-13.3	29.7(1.4) 26.9-32.5	7.99(0.05) 7.90-8.10

[a] NH_3-N flux = (14/17) NH_3 flux

[b] Units of flux are μg m^{-2} min^{-1}

[c] Measured in °Celcius

[d] Numbers in parenthesis represent one standard deviation

[e] Represents range of values

[f] NH_3 concentration was above maximum range on the ammonia analyzer and so maximum and average flux values are unknown.

For NH_3-N, the concentration exceeded the maximum value (20,000 ppb) on the analyzer during most of the summer experiment. The average daily flux value of 4294 μg-N m^{-2} min^{-1} includes maximum measured concentrations and is reported only to demonstrate the dramatic increase during the warmest months. This should not be considered a true flux value. The actual flux is assumed to be higher, but the extent of the increase is unknown. Aneja *et al.* (2000) reported a range of ammonia flux values of 2358-8526 μg-N m^{-2} min^{-1} from another hog lagoon in North Carolina during the summertime.

Lagoon samples were collected daily throughout each experimental period at the surface near the experimental chamber system and simultaneously at a randomly chosen location at the lagoon. The samples were compared to check for differences in concentration levels between the fixed chamber location and other random locations where effluent samples were collected. Using SAS Statistical Software Version 8.2 (SAS Institute, Cary, NC), an independent samples t-test was performed (n = 23) and it was determined that there was no significant difference (p-value > 0.05) in concentration (mg/L) for any of the lagoon samples (sulfide, TAN, TKN). It is therefore assumed that the concentration levels are relatively uniform throughout the lagoon surface and that the emissions measured at the chamber locations represent the average emissions from the entire lagoon surface. The average daily emission from the 3.06-ha lagoon during the summer is calculated to be more than 189 kg day^{-1} for NH_3-N and 230 g day^{-1} for H_2S.

Barn Emission Rates

A Teflon® sample line was inserted inside the chimney of the first 92 cm fan to turn on in series in order to measure NH_3-N and H_2S gas concentrations at the fan ventilation exhaust. Concentration measurements for NH_3-N were highest during the winter and spring, 8.9 and 8.4 ppm, respectively. The higher concentration values during the winter may likely be attributed to less airflow through the building since the ambient and barn temperatures were generally cooler and the fans are staged to turn on as temperatures increase. A buildup of the gas therefore occurs in the building with fewer fans operating. During the spring, the average hog weight was ~88 kg as compared to 38-58 kg during the other seasons when measurements were made. It is expected that the large concentrations measured in the spring are due to the age and weights of the animals housed in the barn. The highest average concentration for H_2S (673 ppb) also occurred during the winter. This value is well below the 500 ppm concentration level at which the CDC reports that severe health risks may occur but well within the odor threshold range (ATSDR, 2004).

Table 2. Statistical summary table of total and normalized average daily NH_3-N and H_2S barn emission rates for each season

	Total Emission Rate[a]			Normalized Emission Rate[a,b]		
Season	Mean[c]	Minimum	Maximum	Mean[c]	Minimum	Maximum
NH_3-N						
Winter 2005	3260 (2156)	54	8930	33.5 (22.1)	0.6	91.7
Spring 2005	4508 (1652)	1550	14514	30.5 (11.2)	10.5	98.2
Summer 2005	1643 (796)	628	8935	24.2 (9.2)	9.2	131.6
Fall 2005	890 (552)	299	3027	11.6 (7.2)	3.9	39.4
H_2S						
Winter 2005	407 (212)	0	911	4.2 (2.2)	0.0	9.4
Spring 2005	482 (142)	100	859	4.3 (1.0)	0.7	5.8
Summer 2005	83 (49)	2	287	1.4 (0.7)	0.0	4.2
Fall 2005	134 (40)	1	252	1.7 (0.5)	0.0	3.3

NH_3-N flux = (14/17) NH_3 flux

[a] Units of flux are g day^{-1}

[b] AU (Animal Units) = 500 kg Live Animal Weight

[c] Numbers in parenthesis represent one standard deviation

Total and normalized emission rates for both NH_3-N and H_2S are given in Table 2. Calculated total emission rates for both NH_3-N and H_2S were highest during the spring, 4508 and 482 g day^{-1}, respectively. Emissions were lowest during the fall season for NH_3-N (890 g day^{-1}). The average emission rate for each season was normalized by 500 kg LAW, thus removing the total live mass as a variable to explain emission rates. Normalizing the data also provides an effective means to compare emission rates with other studies. The normalized emission rates ranged from 11.6-33.5 g day^{-1} for NH_3-N and 1.4-4.3 g day^{-1} for H_2S. It is likely that other factors such as climatic conditions, animal activity, and/or length of time the animals have been housed in the barn may affect the emission rates.

Conclusions

Emissions of atmospheric NH_3-N and H_2S from a commercial anaerobic swine waste treatment lagoon and a fan-ventilated swine confinement building located next to the lagoon were measured over a one year period. Continuous simultaneous measurements were made at the lagoon using a dynamic flow-through chamber system and at the barn ventilation exhaust for ~1 week each during four seasons in an effort to examine diurnal and seasonal variability.

Lagoon flux was highest for both NH_3-N and H_2S during the summer sampling initiative. The NH_3-N measurements surpassed the instrumentation maximum value (20,000 ppb) during most of the summer experiment. Generally, the NH_3-N emissions were ~3-4 orders of magnitude greater than H_2S. The average daily emission from the 3.06-ha lagoon during the summer was more than 189 kg day^{-1} for NH_3-N and ~230 g day^{-1} for H_2S. The lowest fluxes were measured during the winter.

At the barn fan exhaust, the highest emission rates from the barns were measured during the winter and spring for both NH_3-N and H_2S. The lowest emission rates were measured during the fall for NH_3-N and summer for H_2S.

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Gas Exchange between Canopy and Atmosphere

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Abstract

The paper gives brief descriptions of an inverse Lagrangian model of gas transport in plant canopies and multi-layer models of canopy gas exchange. The inverse Lagrangian model allows the inference of sites of gas exchange in the canopy and their source and sink strengths from measured profiles of gas concentration and statistics of the canopy turbulence. The second model analyses gas exchange in terms of resistances to transport across boundary-layers at leaf and foliage surfaces, and in the case of bi-directional gas fluxes, resistances to further transport through stomata to leaf interiors. Gas diffusion through stomata is controlled by stomatal resistance and the difference between the gas concentrations at the leaf surface and that in the sub-stomatal cavity, known as the compensation point. Coupling of both models is seen as a powerful way to study gas exchange in plant canopies and examples are given of their combined use to study pathways of NH_3 exchange between canopy and atmosphere.

Introduction

Understanding, modelling and measuring the exchange of trace gases between agricultural sources and the atmosphere can be complicated by the fact that the gases may have both sources and sinks within the canopy. Examples include CO_2, NH_3, NO, NO_2 and SO_2. Early attempts to infer source/sink distributions of scalars within crop and forest canopies relied on a classical flux-gradient relationship appropriate for the air-layers above the canopy, in which the flux was calculated as the product of a height-dependent turbulent diffusivity, K, and the mean local concentration gradient of the scalar. The subsequent demonstration that classical K-theory is inappropriate in the canopy space, e.g., Denmead and Bradley (1987), led to the development of alternative approaches. Some of these require high-frequency measurements of scalar concentrations, not yet possible for most of the trace gases of interest to the Workshop. Others, though, rely on mean concentration gradients and the paper is concerned primarily with the application of one of these known as Inverse Lagrangian (IL) analysis which is based on a Localized Near Field (LNF) theory due to Raupach (1989a). It assumes that the scalar concentration profile within the canopy is the result of contributions from both local and distant sources. Transport in the near field close to an emitting surface such as a leaf is described by a Lagrangian dispersion model and that in the far field, say >1 canopy height downwind, by turbulent diffusion following K-theory. Inputs to the analysis are the mean scalar concentration profiles above and within the canopy, certain statistics of the turbulence and an index of atmospheric stability which can have a large influence on the results through its effect on far-field diffusion. The analysis allows us to identify the sites of gas exchange in plant canopies in a non-disturbing continuous way. It is a micrometeorological alternative to cuvettes and chambers. Detailed descriptions of the technique and its practical application have been given by Raupach (1989b) and Denmead et al. (2005). A brief outline is given below.

The paper describes different applications of the IL approach. Most have been concerned with inferring sources and sinks of heat, water vapour and CO_2 within the canopy (Denmead and Raupach, 1993; Denmead et al., 2000; Leuning, 2000; Katul et al., 2001; and Denmead et al., 2005). However, others have examined source-sink distributions for trace gases: ammonia (Harper et al., 2000; Nemitz et al., 2000a; Denmead et al., 2005), methane (Leuning et al. 2000), and radon (Simon et al., 2005). The studies of NH_3 exchange are perhaps of most interest to the Workshop. They reveal a variety of emission patterns and raise the question of how much of the NH_3 released from a ground source (fertiliser, slurry or manure) can be recovered by the canopy as the gas diffuses to the atmosphere. The same question arises for other reactive trace gases such as SO_2 and NO. The paper examines this question as well as the coupling of IL analysis and multi-layer models of canopy gas exchange to understand emission processes for reactive gases.

Inverse Lagrangian Dispersion Analysis

The semi-quantitative description here is a précis of developments by Raupach (1987, 1989a,b). In extensive, uniform plant canopies in steady atmospheric conditions, the conservation equation for scalars becomes

$$S(z) = dF/dz \qquad [1]$$

where S is the source or sink strength for the scalar, z is height above the ground and F is the vertical flux density of the scalar. On integration, Eq. [1] leads to

$$F(z) = F_g + \int_0^z S(z)dz \qquad [2]$$

where F_g is the flux density of the scalar to or from the ground.

The forward Lagrangian approach to turbulent transfer in plant canopies aims to predict the mean concentration profiles of scalars from given source distributions. It does so by tracking an ensemble of "marked particles" carrying the scalar. Turbulent motions in plant canopies are coherent over finite length and time scales so that fluid particle velocities exhibit persistence over significant time intervals. The typical persistence time for the vertical velocity of a wandering element is the Lagrangian time scale T_L. In the near-field close to the source, particle trajectories depart little from straight lines. The mean depth of the cloud generated by the source, σ_z, grows linearly with time, t, and is calculable from a Lagrangian description of the turbulence:

$$\sigma_z(t) \rightarrow \sigma_w t \qquad [3a]$$

with σ_w being the standard deviation of the vertical velocity w. In the far-field some distance from the source, persistence breaks down and particle trajectories resemble random walks, as in a diffusion process; cloud depth increases as $t^{1/2}$.

$$\sigma_z(t) \rightarrow \left[2\sigma_w^2 T_L(t - T_L)\right]^{\frac{1}{2}} \qquad [3b]$$

The near-field extends about one canopy height downwind of a point scalar source such as a leaf.

It is evident that the scalar concentration at any point in the canopy results from both near- and far-field influences, so that the actual concentration C can be split into a far-field component C_f that obeys gradient diffusion, and a near-field component C_n that does not.

$$C(z) = C_f(z) + C_n(z). \qquad [4]$$

Raupach (1989a) shows how both C_f and C_n can be related explicitly to the source density profile in the canopy provided one knows σ_w and T_L. The far-field diffusivity is given by

$$K_f = \sigma_w^2 T_L. \qquad [5]$$

Following K-theory,

$$F(z) = -K_f(z)\frac{\partial C_f}{\partial z}, \qquad [6]$$

which, on integration, leads to

$$C_f(z) = C(z_R) - C_n(z_R) + \int_z^{z_R} \frac{F(z)}{K_f(z)}dz, \qquad [7]$$

where $C\ (z_R)$ is the concentration at a reference level z_R well above the canopy. Raupach (1989a) derives a mathematical expression for C_n involving S, σ_w and T_L which then enables concentrations to be related to source strengths and statistics of the turbulence, specifically σ_w and T_L. In practice, σ_w can be measured directly, but usually, T_L will be inferred from models or theoretical considerations. Raupach (1989a,b) discusses the various assumptions made in the analysis and the sensitivity of the analysis to its parameters, while various forms for the profiles of σ_w and T_L are described in Denmead et al. (2005). To summarise, once σ_w and T_L are known, then C_f and C_n, hence C_z, can be found through LNF analysis for any given source distribution.

The inverse problem is to find the source distribution from a given, measured concentration profile. Raupach (1989b) treats the problem in discrete form. The canopy is divided into m source layers, each with a uniform source density S_j, where $j = 1,\ldots,m$. For simplicity, any flux from the ground is assumed to be lumped in with the source from the lower layer ($j = 1$), although Raupach (1989b) states that this is not a necessary simplification. Scalar concentrations are measured at n heights z_i, the top height coinciding with the reference level z_R well above the canopy, where $C = C_R$. Concentrations at any level are influenced by the sources at all levels. Raupach (1989b) notes that the two sets of heights can be fixed quite independently and need not coincide in any way.

The first step in the analysis is to consider the concentration profile resulting from the uniform release of a scalar tracer in source layer j with source density s in that layer and zero elsewhere. From the developments for the forward problem, the resulting concentrations c_i can be found (Eq.4 and 7 and Raupach's (1989a) mathematical expression for C_n alluded to above). The c_i define a dispersion matrix D with elements D_{ij} given by

$$D_{ij} = \frac{c_i - c_R}{s\Delta z_j} \qquad [8]$$

Each D_{ij} is the concentration at measurement height i produced by a uniform source of unit strength extending through layer j, but zero elsewhere. As Raupach (1989b) observes, the matrix **D** can be calculated by any theory that solves the forward problem and, in particular, by LNF theory given the turbulence parameters σ_w and T_L. Once **D** is known, the concentration profile generated by any source profile S_j is given by the superposition of solutions. Thus

$$C_i - C_R = \sum_{j=1}^{m} D_{ij} S_j \Delta z_j\ . \qquad [9]$$

Leuning et al. (2000) outline simplified procedures for calculating the D_{ij}.

Raupach (1989b) noted that by choosing $m = n$ so that S_j is sought in the same number of source layers as there are concentration values C_i, Eq.[9] becomes a set of m linear equations which can be solved for the source profile S_j. He pointed out, however, that because small errors in C_i and the turbulence parameters can produce large errors in S_j, it is necessary to include redundant concentrations so that source densities are sought in m layers from n concentrations with $n>m$. He developed a least squares procedure to minimize errors in S_j.

Leuning (2000) introduced additional parameterizations to account for the effects of stable and unstable atmospheric conditions on σ_w and T_L. Stability has been shown to have quite large effects on the analysis. Leuning (2000), for instance, showed that in nighttime stable conditions, applying stability corrections reduced the predicted net fluxes of water vapour and CO_2 from a rice crop by >50% and gave results which agreed very well with independent measurements of the fluxes by eddy correlation, while Denmead et al. (2005) found increases of 30 to 40% in predictions of the net fluxes of heat, water vapour and CO_2 from a wheat canopy through applying Leuning's corrections in daytime unstable conditions, and similarly good agreement with eddy correlation measurements. Denmead et al. (2005) concluded that the stability correction scheme of Leuning (2000) is both adequate and necessary.

Denmead et al. (2005) discuss practical considerations in the application of inverse Lagrangian analysis. These include:

- the need for extensive, horizontally uniform canopies,
- the need to have more concentration measurements than source layers (8 conentration measurements and 4 source layers seems to be a reasonable sampling scheme),
- the need for correct specification of the T_L profile (the most successful are forms of the T_L profile in which T_L decreases with depth in the canopy),
- the need to take account of atmospheric stability,
- instrumental needs (using just one instrument to make the same measurement at all levels wherever possible).

Gas Exchange in the Canopy

There are many multiple-resistance analog models of canopy gas exchange which can be used to predict or measure source-sink distributions. Of particular interest here are models for bi-directional fluxes. Relevant examples are models of NH_3 exchange due to Sutton et al. (1995), Asman et al. (1998) and Nemitz et al. (2000b). These envisage NH_3 diffusing from some reference point above the canopy to the surface of a leaf through an aerodynamic resistance R_a and a leaf boundary-layer resistance R_b (using the terminology of Sutton et al. (1995)). They invoke the concept of an ammonia compensation point, χ_s, originally proposed by Farquhar et al. (1980). At the single leaf level, the compensation point is the NH_3 concentration within the leaf sub-stomatal cavity that is in equilibrium with the $[NH_4^+]$ in the leaf apoplast, governed by temperature and pH. If the NH_3 concentration in the air surrounding the leaf, $\chi(z)$ is higher than the compensation point, NH_3 is taken up by the leaf by diffusion through stomata with resistance R_s; if it is less, NH_3 is lost from the leaf by the same pathway. The flux of gas to or from the leaf is described by

$$F_g = (\chi_s - \chi(z))/(R_a(z) + R_b + R_s). \qquad [10]$$

The resistances R_a and R_b can be determined from wind and temperature profiles and R_s can be measured with a diffusion porometer.

Ammonia can also be adsorbed by dew and thin water films on leaf cuticles and subsequently desorbed. Cuticular leaf exchange is generally modeled as diffusion to or from the leaf surface across the leaf boundary layer and a cuticular resistance R_w. The concentration of NH_3 at the leaf surface is assumed to be zero. The concentration of NH_3 about the leaf, χ_c, is given by

$$\chi_c = \frac{\chi(z)(R_a(z) + R_b)^{-1} + \chi_s R_s^{-1}}{(R_a(z) + R_b)^{-1} + R_s^{-1} + R_w^{-1}}, \qquad [11]$$

and the canopy flux F_c by

$$F_c = -\frac{\chi_a - \chi_c}{R_a(z) + R_b}. \qquad [12]$$

Nemitz et al. (2000) describe how to extend this one-layer leaf model to a multi-layer canopy model with emission from a ground source. The extension will not be detailed here.

The same model is applicable to the exchange of other trace gases relevant to air quality. Conrad and Dentener (1999) list typical compensation points for soil and vegetation for selected trace gases. As well as NH_3, the list includes CO, OCS, NO, NO_2. We can add to these CO_2, for which the compensation point depends on whether the plant has a C3 or a C4 pathway, and SO_2 and O_3 for which the compensation points are generally assumed to be zero (Baldocchi et al., 1989; Asman et al., 1998). The necessary changes for those gases for which no compensation points exist are obvious.

Bi-directional Ammonia Fluxes

It is evident from the foregoing sections that coupling micrometeorological analyses of source-sink distributions in canopies with multi-layer models of gas exchange can provide a powerful tool for studying processes of canopy exchange, since it can identify not only the exchange sites and their source-sink strengths, but also the soil and plant processes involved. This is particularly useful for bi-directional fluxes. Published studies of NH_3 exchange provide some good examples. Harper et al. (2000), Nemitz et al. (2000a,b) and Denmead et al. (2000, 2005) have used both IL analysis and canopy gas exchange models to study pathways of NH_3 exchange in plant canopies. These investigations reveal various source-sink patterns for NH_3 emission and transport and permit an evaluation of the ability of plants in the canopy to trap NH_3 emitted from the soil.

Harper et al.(2000) examined the emission of NH_3 following overhead sprinkler application of dairy effluent to a dense corn crop 3.3m high with a leaf area index (LAI) of 5. The expectation was that most of the ammonia emission would be from the soil surface and that because of the high concentrations generated in the canopy space following the application of effluent, there could be substantial recapture of the emitted NH_3 by the foliage. The IL analysis indicated that although very high concentrations occurred in the canopy after the application (in excess of 400 $\mu gN\ m^{-3}$ immediately afterwards), very little NH_3 was recaptured. In one observation period, for instance, some 17% of the NH3 emitted from the soil was recaptured in the first hour after application, but the soil emission decreased subsequently and the foliage became a net NH_3 source. Overall, only 21% of the net emissions came from the soil and 79% from the foliage. Apparent compensation points calculated from Eq. [10] exceeded published values for corn by one to two orders of magnitude. It was concluded that NH_3 losses from the plants were predominantly from the foliage rather than by diffusion from leaf interiors. This suggests that ammonia-releasing residues can remain on the leaf surface for many days after effluent application.

Nemitz et al. (2000b) examined NH_3 exchange in a canopy of oilseed rape, 1.38m tall with an LAI of 5.3. Their IL analysis indicated that the litter layer on the ground surface was a source of NH_3, but all the NH_3 emitted from the litter was recaptured in the lower half of the canopy. The exchange of NH_3 with the atmosphere was governed by the top 0.5m of the canopy, which constituted a second source. The NH3 compensation points for leaves in this layer, calculated from measurements of apoplastic $[NH_4^+]$ and pH, indicated that no significant stomatal emission should have occurred, suggesting that the seed cases in the layer were the source of the NH_3 emitted to the atmosphere.

Denmead et al. (2005) report an analysis of emissions of NH_3 from a crop of sugarcane for several days after urea fertilizer was spread onto a trash mulch on the soil surface. The crop was 0.8m tall with an LAI of only 1.4. The IL analysis indicated that the foliage recaptured only 6% of the N emitted from hydrolysis of the urea despite the development of quite high NH_3 concentrations within the canopy, typically around 100 $\mu gN\ m^{-3}$. The resistance analog model of canopy gas exchange confirmed the rates of leaf uptake inferred from the IL analysis when the rates were small ($<1\ \mu gN\ m^{-2}\ s^{-1}$), but predicted much higher uptake rates than the IL analysis when they were $>2\ \mu gN\ m^{-2}\ s^{-1}$. The authors suggest that the discrepancy could be due to the very high rates of NH_3 uptake creating non-equilibrium conditions in the leaves because of the slow translocation of the absorbed NH_3. It should be noted that the concentrations of NH_3 within the canopy and the rates of leaf uptake observed here were orders of magnitude higher than those reported by Nemitz et al. (2000a). The ability of the canopy to recapture substantial amounts of NH_3-N emitted from fertilizer or plant residues at the ground is an important question in agricultural air quality that is still undecided.

It should be said that in all three of the examples considered above, the IL analysis predicted net canopy exchanges of NH_3 that were in excellent agreement with independent micrometeorological measurements in the air layer above the canopy, but this is not its primary purpose. The real benefit of the analysis is its ability to provide detailed information on the magnitude and distribution of scalar sources and sinks within the canopy in a non-disturbing, continuous way. When coupled with multi-layer canopy models of gas exchange, it provides a valuable tool for understanding and determining the many pathways by which reactive trace gases, and NH_3 in particular, are exchanged between canopy and atmosphere.

Conclusions

Coupling the IL analysis with canopy gas exchange models has demonstrated the existence of several different pathways for NH_3 exchange in the canopy, some expected, some not. They include long-lasting volatilization from residues of effluent sprinkled on the foliage, volatilization from fertilizer and plant residues at the ground surface; some of the canopy acting as an NH3 source, some of it as a sink; losses from foliage elements other than leaves, such as seed cases,; and absorption by canopy foliage. Just how efficient foliage absorption is in recapturing NH_3 volatilized from sites within the canopy remains an open question. The evidence is that recovery can be as much as 100% when volatilization rates (and canopy gas concentrations) are small, but it decreases as volatilization rates increase. Similar questions arise for other reactive gases such as SO_2, NO and NO_2: how much of the SO_2 deposited on canopies is absorbed by the foliage, how much reaches the ground; are chamber measurements of NO and NO_2 emissions from the ground good indicators of how much is emitted to the atmosphere? The models described here provide very useful tools for answering such questions.

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The Surface Boundary Layer of a Cattle Feedlot: Implications for Long-term Measurement of Ammonia Fluxes

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Abstract

Emissions of ammonia and other traces gases from cattle feedlots can impact air quality at local and regional scales. Unfortunately, there is uncertainty in current estimates of feedlot emissions, much of which stems from inadequate field measurements. Micrometeorological techniques are appealing choices for measuring trace gas losses because they: (1) integrate over large areas, (2) do not disturb the surface or affect aerodynamic transport, and (3) can conceptually be operated for long time periods on a near continuous basis. Regrettably, many micrometeorological methods are ill-suited for work at feedlots because of the potential for spatial variation in fluxes across the surface and inadequate upwind fetch. Furthermore, it is difficult to evaluate the potential of different methods because the characteristics of the surface boundary layer above feedlots have not been studied in detail. In this project, sonic anemometers and fast response gas analyzers were used measure the turbulent regime above a large commercial feedlot in Kansas. Data showed how weather, topography, pen surface conditions, and other factors affected the surface boundary layer. Analyses included the effect of advection arising from non-homogenous emissions as well as errors induced by sloping or hilly terrain. Results from the boundary layer study were used to evaluate the feasibility of different flux measurement techniques, including: the modified Bowen ratio, flux profile methods, conditional sampling, and relaxed eddy accumulation. Partitioning of ammonia flux into gaseous and aerosol components was included in the analysis. A central goal was to predict which technique, in theory, would be best for obtaining near continuous ammonia flux data over long time periods (e.g., one year). Development of these techniques is needed to improve measurement and modeling of the feedlot nitrogen balance. Determining the fate and transport of all nitrogen used in the feedlot operation is central to quantifying long-term environmental impacts.

An Integrated Approach to Measuring Emissions from Confined Animal Feeding Operations at the Whole Facility Scale

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Abstract

Agricultural operations produce a variety of particulates and gases that influence air quality. Agriculture, through wind erosion, tillage and harvest operations, burning, diesel-powered machinery and animal production operations, is a source of particulate matter that can enter human lungs and cause pulmonary problems. Animal production operations can be a source of gaseous emissions such as ammonia, odor-causing volatile organic compounds, hydrogen sulfide, greenhouse gases (methane, nitrous oxides) and airborne pathogens. These emissions can negatively impact human health, property values, and the environment. The presence of buildings and other structures often make whole facility measurement capability a requirement for understanding the source strength and characteristics. The ability to use standoff methods to determine the movement and concentrations of emissions on a whole facility basis opens new capabilities for model development and verification.

An integrated system to measure whole facility emission was designed to characterize the complex structures and temporally dependent emission rates often associated with production operations. This approach combines state of the art standoff measurement techniques with standard point source monitoring equipment to provide the calibrated, high spatial and temporal frequency data required to develop and validate the models required for emission reduction and regulation. This effort includes the design, construction and operation of a new multi-wavelength lidar developed to map and track particle emissions. The lidar incorporates a laser emitting simultaneous, pulsed NdYAG laser radiation at 355, 532 and 1064 nm at a pulse frequency of 10 kHz. The system also includes open path FTS measurements for integrated chemical concentrations, and state-of-the-art point measurements of turbulence, particulate and gas concentrations.

This approach was evaluated in a multidisciplinary atmospheric study at a swine production farm in Iowa. Aerosol plumes emitted from the facility were prominent phenomena, and their variations with temperature, turbulence, stability and feed cycle were studied, using arrays of particle samplers and turbulence detectors. Other lidar measurements focused on air motion as seen by long duration scans of the farm region. Successful operation of this system confirms the value of the multidimensional approach for the determination of agricultural emissions in the complex terrain often accompanying production facilities.

Lidar Studies

Emissions of gases and particulates from animal production facilities are of concern because of the potential environmental and health implications. However, the measurement of the emission rate of different gases or particulates has proven to be difficult because of the differences among facilities, variations within a facility caused by differences in building management (ventilation fans), and the interactions among buildings caused by the altered wind flow regime induced by buildings in close proximity to one another. Observations of ammonia concentration observed at different distances and heights above the ground surface adjacent to a 400 head grow-finish swine production facility throughout a production cycle revealed large variations within a day and among days (Hatfield and Pfeiffer, 2005). Much of this variation could not be explained by simple differences in wind speed or wind direction. This prompted a study that utilized a lidar system to measure the dispersion of particulates from this facility coupled with detailed measurements of the turbulence components of wind (Eichinger et al., 2005, Unpublished data).

The use of the lidar system to measure the complete air volume above this facility began to reveal the complexity of air flow and dispersion surrounding production facilities. It was observed that the vertical velocities of wind were 1-5 m s-1, which is much larger than expected. The turbulence regime surrounding the buildings was extremely variable depending upon the wind direction. These observations revealed how quickly a plume of particulates was emitted and dispersed from the facility (Eichinger, W., 2005, Unpublished data). These observations also began to reveal that single point observations located adjacent to a facility may not be capturing the air volume required for an accurate measurement of the emission rates.

These preliminary studies have prompted the development of a more sophisticated lidar system to provide a measure of the particulate size fraction and potentially the gaseous composition of the air volume surrounding an animal production facility. To more accurately quantify the emissions from animal facilities it is necessary to quantify the turbulence regime in order to understand the rate and pattern of dispersion and couple these mechanisms with an improved estimate of the composition of the atmosphere. The goal of these studies is to describe the development of an improved method to quantify the emission rates and dispersion patterns from animal production facilities.

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Workshop on Agricultural Air Quality

New Measurement Protocol for the Determination of NH_3 Emission Factors from Animal Houses in the Netherlands

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Abstract

The Dutch government uses ammonia emission factors, which are determined according to standardized measurement protocols, to assign year-averaged ammonia emission levels to specific animal housing systems and animal categories. This protocol relies on intensive measurements at a single location, and therefore provides a large amount of data that can be used to study the factors controlling the ammonia emission processes. However, the costs of these measurements are usually large. In addition, this approach does not take into account the effect of farm management on the ammonia emission that apperars to be a major variation source and restricts the accuracy of the current single location based protocol.

To deal with these problems, a new measurement protocol has been proposed, which is based on measurements on a larger number of animal houses with the same housing system. In addition, continuous measurements are no longer required. Instead, daily averages could be used, which decreases the requirements for the equipment used in the measurements. Besides, the proposed measurement protocol requires only a limited number of measurement days per location, equally distributed (but at random) over the whole year, to take seasonal effects into account.

Introduction

The deposition of ammonia (NH_3) and ammonium (NH_4^+) can cause a large number of environmental problems, including soil acidification, eutrophication, nitrogen leaching into groundwater and loss of biodiversity (Heij and Schneider, 1991; Bobbink *et al.*, 1992). To reduce NH_3 emissions, emission ceilings have been assigned for all EU member states (EU, 2001). In order to comply with the emission reduction assigned to the Netherlands, development of new measures is needed, which should be supported by fast and accurate measurements to arrive at new estimates of the NH_3 emission factors from each agricultural source.

Agriculture is, by far, the most important contributor to the total NH_3 emission in the Netherlands, with emissions from animal housing and after the application of manure being of particular importance (Sliggers, 2001). To determine the yearly NH_3 emission from specific animal housing systems and animal categories, NH_3 emission factors are usually applied. The measurement protocol used to establish these emission factors (Anonymous, 1996) relies on intensive measurements at a single location. This sampling scheme provides useful information to study the factors that influence NH_3 emissions. However, it only takes variation within an animal house into account, and neglects the possible importance of management variation between different farm locations with the same housing system, which has proven to be an important variation source for odor (Ogink and Klarenbeek, 1997). Besides, costs of these measurements are high, which restricts the number of new animal housing systems that can be measured and therefore limits the development of new and better housing systems.

To deal with these problems a new measurement protocol has been proposed. The objective of this paper is to summarize the basic pillars on which this protocol has been funded.

Methods

To quantify and assess the importance of the different sources of variance associated with NH_3 emission measurements from animal houses, a statistical analysis was performed. First of all, all available datasets were classified according to the following aspects:

- Animal category
- Housing system (per animal category)

- Measurement method and strategy used for the measurements

Then, the emission data (daily averages) were transformed to natural logarithmic values to obtain a normal distribution with dispersion independent of the emission levels (De Boer and Ogink, 1994). The transformed data were analyzed with the REML (Residual Maximum Likelihood) directive of the GENSTAT 6.1 (6th edition) statistical package, to quantify the following sources of variance:

- Variance between farms (σ^2_b)
- Variance within a farm (σ^2_w)
- Variance of measurement equipment (σ^2_m)

Finally, the total variance (σ^2_t) associated with measurements according to a specific sampling scheme was determined by using a model developed by Ogink and Klarenbeek (1997) for odor emissions:

$$\sigma_t^2 = \frac{\sigma_b^2}{k} + \frac{\sigma_w^2}{k \cdot l} + \frac{\sigma_m^2}{k \cdot l \cdot m}$$

With k the number of farms, l the number of measurements (sampling days) within a farm, and m the replicate number of measurements at a sampling day.

Seasonal effects and effects of growth cycles on emission patterns were investigated by expressing daily emissions as a percentages of the average emission (over year or growth cycle), and studying the relative patterns in time.

Results and Discussion

Analysis of all available datasets for fattening pigs and sows shows that not only the variation within the animal house, but also the variation between farms is of importance (Mosquera and Ogink, 2004). In contrast, the accuracy of the measurement equipment used for the measurements seems to have relatively low importance. In order to improve the accuracy of the emission measurements (more accurate emission factor), it is advised to increase the number of locations to be measured rather than to increase the number of measurements in a particular location or to improve the accuracy of the measurement equipment. Therefore, continuous measurements are no longer necessary, and the number of measurement days per location can be largely reduced (Vranken *et al.*, 2004). Besides, since the requirements for the equipment can be reduced, alternative methods (Mosquera *et al.*, 2002, 2005) can be applied. Since some factors affecting NH_3 emissions from animal houses follow a diurnal pattern, use of daily averages is highly recommended. Analysis of growth cycles of fattening pigs and emission showed consistent strong linear relationships. The available emission data were not sufficiently even distributed over the seasons to allow for a clear identification of seasonal effects on emissions. However we surmise that such effects do exist, and may differ between animal categories In order to take potential seasonal effects into account in sampling strategies, a year-round sampling strategy is advised.

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Impacts: Fate and Deposition

Trends of Nitrogen and Sulfur in U.S. Precipitation — the Roles of Combustion-Related and Agricultural Emissions

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Abstract

For more than a quarter century, the National Atmospheric Deposition Program - National Trends Network (NADP-NTN) has measured the acids, nutrients, and base cations in U.S. precipitation. NADP-NTN data are used to evaluate regional and seasonal variations and long-term trends in precipitation chemistry. Trends result from the combined effects of changes in natural and human-induced pollutant emissions, physical and chemical transformations, and weather.

Results of a Seasonal Kendall Trend test of 1985 - 2004 NADP/NTN data demonstrate that statistically significant trends have occurred in the chemistry of U.S. precipitation. Over this 20-year period, dissolved inorganic nitrogen concentrations (nitrate-N + ammonium-N) decreased in the northeastern U.S. and increased in mid-continental states from eastern Washington, Oregon, and California to the Mississippi River Valley. In these mid-continental states, both ammonium, largely from agricultural sources, and nitrate, largely from combustion sources, increased at most sites. In contrast, sulfate concentrations decreased throughout much of the continental U.S.

This paper will examine the roles of combustion-related and agricultural emissions, as well as the changing relationships between airborne nitrogen and sulfur species in affecting these trends.

Introduction

Widespread, statistically-significant increases in ammonium concentrations in precipitation have occurred throughout much of the continental United States (Lehmann et al., 2005). The figure, below, displays the direction and magnitude of Sen's median estimators of the 20-year (1985-2004) ammonium concentration trends at 159 NADP/NTN sites (Lehmann et al., 2006). Upward trends are largest in mid-continental states, where there is a large area with increases exceeding 50 percent (>2.5 percent per year). Throughout much of this area, sulfate concentrations decreased (Lehmann et al., 2005; Lehmann et al., 2006).

Ammonium and sulfate react to form stable submicron aerosols that can be transported long distances (> 500 km) in the atmosphere. The relative amounts of these species affect the chemical makeup of the aerosols, but under atmospheric conditions the various combinations of ammonium and sulfate are stable. Once the ammonium concentration exceeds the amount that will combine with sulfate, the excess can form ammonium nitrate, a labile aerosol at equilibrium with gas-phase ammonia and nitric acid (Seinfeld and Pandis, 1998). These gases are highly soluble, increasing the likelihood of being deposited short (< 500 km) rather than long distances from the source before deposition. Modeling results have indicated that when sulfur and nitrogen oxide emissions are reduced in relation to ammonia emissions, ammonia remains in the reactive gas phase, significantly reducing the transport distance and leading to local deposition (Hov and Hjollo, 1994).

Sulfate decreases, accompanying recent sulfur oxide emissions reductions (Lynch et al., 2000), have resulted in an increase in the number of precipitation samples in which the chemical equivalents of ammonium exceed sulfate (Lehmann et al., 2006). This shift from an atmosphere with a sulfate excess to one with an ammonium excess can affect ammonium deposition patterns, possibly resulting in increased deposition close to sources.

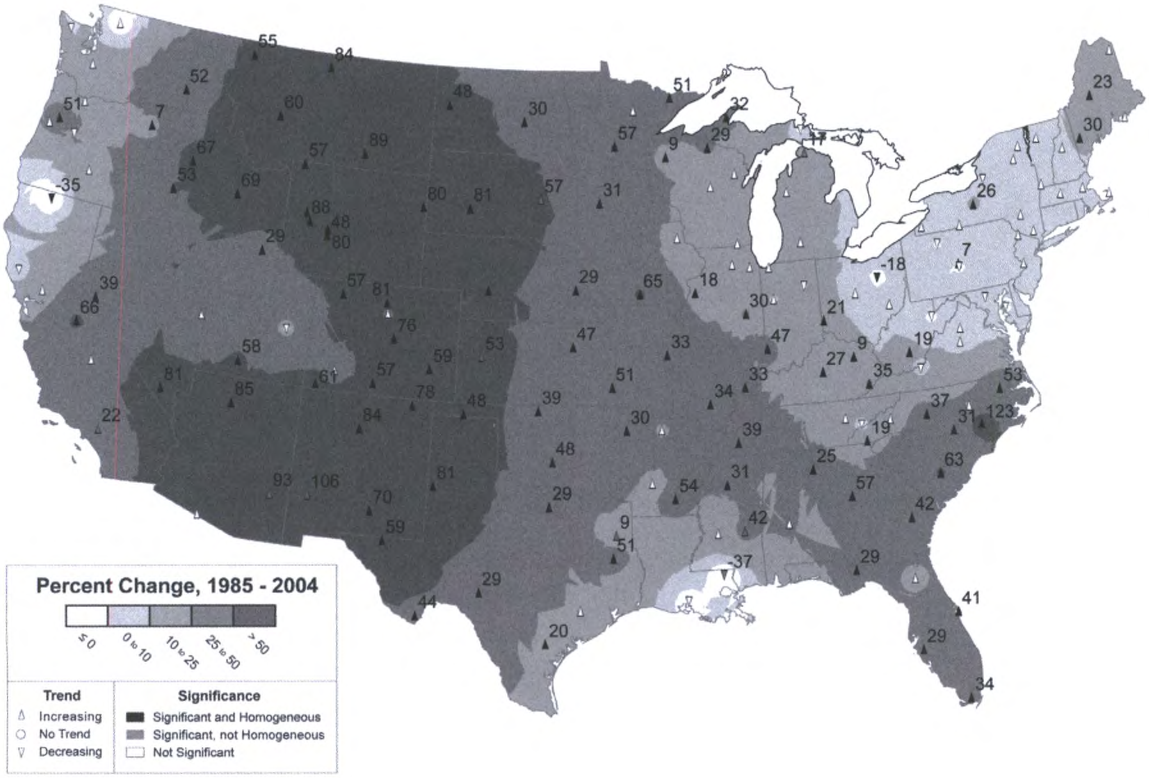

Figure 1. Ammonium concentration trends in precipitation at 159 NADP/NTN sites (Winter 1985 – Fall 2004). Symbols display trend significance ($p \leq 0.10$) and seasonal homogeneity ($p > 0.10$). Numbers display percent changes (Sen's estimators), where trends are significant.

Methods

This paper will report the 20-year concentration and deposition trends of sulfate, ammonium, nitrate, and dissolved inorganic nitrogen (ammonium-N + nitrate-N) in precipitation. Sulfate and nitrate are related to emissions of sulfur and nitrogen oxides, which originate mostly from fuel combustion. Trends of sulfur and nitrogen oxide emissions will be compared with trends of sulfate and nitrate in precipitation. Ammonium in precipitation is related to ammonia emissions, which originate mostly from agricultural activities, and to the relative amounts of gaseous ammonia or particulate ammonium sulfate or ammonium nitrate that are captured in and below clouds. Trends of ammonium in precipitation will be compared with trends of ammonia emissions, as well as changes in the physical and chemical forms of ammonia/ammonium scavenged by precipitation.

Neither of the large regional or U.S. national air quality networks (Clean Air Status and Trends Network, Interagency Monitoring of Protected Visual Environment network) measure gaseous ammonia, nor do they discriminate between particulate ammonium sulfate or ammonium nitrate measurements. As a consequence, it is not possible to examine changes in airborne ammonia and ammonium on a regional or national scale. Instead, changes in the ratio of ammonium to sulfate in precipitation will be used to infer changes in the relative amounts of gaseous and aerosol ammonium. In addition, it is not possible to track changes in ammonia emissions over the 20-year trend period (1985-2004) examined in this paper. The U.S.

Environmental Protection Agency (EPA) only started reporting ammonia emissions estimates in 1990. To complement the EPA estimates, ammonia emissions will be calculated using the Carnegie Mellon Ammonia Model (Carnegie Mellon University, 2004), which combines emission factors and agricultural activity (e.g., numbers of cattle, swine, poultry, and dairy and amount of fertilizer applications) to compute emission fluxes.

Together, the emissions and air chemistry changes will be used to evaluate the cause of reported ammonium wet deposition trends.

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Reactive Nitrogen Species and Nitrogen Deposition in the North China Plain

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Abstract

The North China Plain (NCP) is called the granary of China since it provides more than 30% of China's total wheat and corn production. Winter wheat – summer maize crop rotation systems with nitrogen applications of up to 600 kg N ha^{-1} yr^{-1} are most common. The nitrogen efficiency of these crop rotations is often below 30% and considerable amounts of nitrogen are lost both by leaching and by emission of gaseous nitrogen species. These emissions from crop rotations, together with emissions from animal husbandry and with growing emissions of oxidised nitrogen species from traffic exhaust, are expected to generate high atmospheric concentrations of reactive nitrogen species and high amounts of nitrogen deposition. A monitoring network for wet and dry deposition of nitrogen was established at several locations in 2003. Here we present recent data on atmospheric concentrations and deposition of reactive nitrogen species in the NCP and report on approaches involving plants for the biomonitoring of N deposition.

Introduction

During the last decade China's economic growth has been much faster than in most other countries, which lead to alarming levels of environmental pollution in some regions (He et al., 2002). Also agriculture experienced major changes in the past years, with the North China Plain (NCP) being the largest and most intensively used agricultural region.

The current situation of China's agriculture is rather intricate. On the one hand a growing population demands an increasing food production, which can only be met by reaching a higher productivity of the sector. On the other hand the availability and sustainability of arable land is limited and in some regions it is decreasing with the ongoing urbanisation.

At present China is the country with the highest consumption of N-fertilisers in the world and the excessive and unbalanced use of mineral fertilisers is a major environmental concern (Pacholski, 2003). At the same time the increasing car fleet causes traffic related problems and increasing emissions of oxidised nitrogen. In Beijing alone, the number of vehicles increased by a factor of 4 from 0.66 million in 1994 to 2.6 million in 2005 and vehicle emissions of NO_x and particulate matter (PM) are expected to further increase. Besides the traffic, industrial facilities and co-generation power plants may be regarded as the most important sources of urban air pollution. Energy use and air pollution have been synonymous in China for decades, especially in urban areas. In rural areas, air pollution is also severe because a significant amount of industry that is highly dependent on coal as an energy source is located in the countryside (Tang, 2004).

The study region (NCP) is indicative of all the ecological and health related problems listed above. It is called "China's granary" because it has the highest agricultural productivity nationwide with a dominance of double cropping systems involving winter wheat and summer maize. It provides approximately 41 % of wheat and 25 % of maize yield of China's total grain yield (Böning-Zilkens, 2004).

Extensive and non-sustainable nitrogen fertilizer applications of up to 600 kg N ha^{-1} yr^{-1} are most common. However, the nitrogen efficiency of the crop rotations is often below 30% and considerable amounts of nitrogen are lost both by leaching into the groundwater and by emission of gaseous nitrogen species into the atmosphere.

The NCP is located at the east of Taihang and Funiu mountains, covering parts of the provinces of Beijing, Hebei, Tianjin, Shandong, Henan, Anhui and Jiangsu. This means not only emissions from fertilised and manured fields but also emissions from animal husbandry in NCP particularly in the surroundings of Beijing contribute to the high loads of reduced nitrogen. Being mixed with the NO_x-emissions from industry and traffic, these emissions are expected to generate high concentrations of reactive nitrogen species and high deposition loads (Galloway, 2003).

Up to now reliable estimates of NO_x and NH_y in the NCP are largely lacking, and a monitoring network comparable to European (e.g. Schmitt et al., 2005) or US standards does not yet exist. The present study thus aims to monitor air pollution and nitrogen deposition and its effects in the NCP.

Material and Methods

The total nitrogen deposition in the NCP is being investigated in the framework of an international DFG-funded research training group performed by China's Agricultural University (CAU) and the University of Hohenheim, Germany (http://rtgchina.uni-hohenheim.de). The project is divided into three parts addressing wet deposition, dry deposition and effects related bioindication.

A monitoring network for bulk nitrogen deposition was established in the NCP in 2003 with 15 stations. Bulk deposition is routinely monitored similar to Europe using standard rain gauges (SDM6, Tianjin Weather Equipment Inc., China). In addition, in 2004 three monitoring stations have been equipped to monitor wet-only deposition using an Auto Precipitation and Dust Sampler (APS-III, Wuhan Tianhong Inc., China).

Measurements of both the gaseous and particulate nitrogen species have been commenced in 2005 in order to investigate dry deposition. In different locations at three experimental farms of the CAU we operate passive samplers (Radiello) to measure ammonia on a fortnightly basis. Furthermore, a High Volume Sampler (Digitel DHA-80) has been installed to collect total suspended particulate matter (TSP), PM10 and PM2.5 at a site near Beijing. In spring 2006 a nitrogen oxide analyzer will be installed as well.

In order to study the effects of nitrogen deposition an active biomonitoring system was tested in 2005 at the three sites in NCP and at various locations in SW-Germany. Clones of a European grass species, which is known to have spread in past decennia in regions with high nitrogen deposition loads, were used for these experiments (using the system of VDI, 2003). We wanted to test the hypothesis if unfertilised test plants exposed in the field could use the local nitrogen deposition in order to increase biomass and nitrogen levels (Franzaring & Fangmeier, 2004). Another plant related method applied in the project, is the ITNI ^{15}N-dilution technique similar to the method developed by Mehlert et al. (1995) and Russow et al. (2001), which was used to estimate plant (winter wheat and maize) availability and total amount of N deposition at the same three sites as the active biomonitoring system.

Results and Discussion

First results from the monitoring campaigns suggest nitrogen deposition in the NCP to be as high as 70 kg ha^{-1} yr^{-1}. In Beijing, bulk deposition of inorganic N averaged about 30 kg N ha^{-1} yr^{-1} with ratios of NH_4-N to NO_3-N up to 2.2. Inputs of organic N from precipitation were measurable but were much smaller than those of inorganic N. Bulk deposition of N, in particular NH_4-N, was significantly higher than wet-only deposition, indicating substantial contribution of large-size particulate matter (e.g., dust from agricultural activities) to bulk N deposition in NCP. The difference between bulk and wet-only deposition of inorganic N was around 8.4 kg N ha^{-1} during the main rainy season in 2003 and 2004, which was equal to 45% of wet-only N deposition in the same period (Liu et al., 2006, in press). Obviously, as part of dry deposition, the additional N in bulk deposition relative to wet-only deposition mainly derived from large-size PM or dust, whose fall-down is driven by gravity. The initial results suggest that dry deposition of N was substantial in NCP in particular Beijing.

The levels of particulate matter (PM10) exceed European (50 $\mu g\ m^{-3}$) and even Chinese (150 $\mu g\ m^{-3}$) thresholds by far. Also the EU standard for the number of tolerated daily exceedances is not met in the Beijing area. Results of our PM10 measurements showed 125 exceedances of the daily mean European threshold during only five months. In comparison the quantity of exceedances of the European daily mean threshold in rural European regions is less than 20 times per year (BUWAL, 2005). The maximum daily mean of 429 $\mu g\ m^{-3}$ also reflects the high PM peak concentrations in Beijing area. Although the PM monitoring site is located in an agricultural setting we note that the air quality at this site is much affected by air masses from the nearby Beijing mega city. Primary pollutants (NO_x, VOCs, SO_2 and TSP) from the city and their secondary products (ozone and secondary particulates) will thus also be present here. This is indicated by the high concentrations of PM2.5, which is normally made up from secondary particulates. Analyses of the chemical composition of the PM10 samples are on the way to characterize the major sources of the dry particulate deposition. First results indicate that there is not much nitrogen present in the PM10 fraction. However, other particle associated pollutants (heavy metals and organic compounds) may pose ecological and health risks in this area.

In order to also address the gaseous dry N-deposition we determined ammonia concentrations at various sites in the NCP. The levels showed strong seasonal and spatial variability and a correlation to the dust loads at the Beijing site. Latter finding indicates that air pollution may be strongly affected by agricultural activities at that site.

Ammonia monitoring and biomonitoring were synchronised in order to study the potential effects of nitrogen deposition to plants. Although not native to China, clones of the bioindicator species survived the exposure in the three NCP locations. However, plants of the temperate grass species were taller in the German locations and plant weight generally declined from north to south due to higher average temperatures and shorter day length at lower latitudes. Average ammonia concentrations at the German reference sites varied from 2.3 to 7.3 $\mu g\ m^{-3}$, which are rather low concentrations just above the background levels. In China seasonal ammonia levels were in the range from 10 to 43 $\mu g\ m^{-3}$, which indicates intensive agricultural activity. While in Germany plant growth parameters (height, dry weight) were not related to the (low) ammonia concentrations, senescence proved to be somewhat retarded in plants exposed to higher ammonia levels. It therefore seems that the availability of airborne reduced nitrogen may increase the vitality or reduce senescence in this plant species. At the Chinese sites, however, where higher ammonia concentrations were recorded, no correlations between ammonia, growth parameters and senescence were identified.

To quantify atmospheric N deposition a ^{15}N dilution technique is being used, which also relies on using plants. Quantification of the total N deposition in NCP with model plants is going on with winter wheat and the analysis of maize is on the way. Final results including both maize and winter wheat will indicate the total airborne N input into a soil-plant system in NCP.

Outlook

As the results on atmospheric N-deposition measured with the presented methods confirm high levels of wet and dry deposition in NCP, we plan to continue the series of measurements in 2006. We will then strongly focus on integrating the different approaches to monitor wet, gaseous and particulate matter deposition and consider the sources and chemistry of nitrogen deposition as well as its relationship to the local meteorology. Furthermore an ecological impact study of nitrogen deposition effects on plants and semi-natural vegetation using suited biomonitoring approaches will be set up.

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Dry Deposition of Ammonia in the Vicinity of a Swine Production Facility

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Abstract

While animal production facilities have been identified as important sources of atmospheric NH3, there are no estimates of local NH3 dry deposition for U.S. sites. Such estimates are necessary to estimate net farm-scale emissions and for assessing the risk of neighboring ecosystems to nitrogen deposition. This project investigates the dry deposition of NH3 around a 5000 head swine production facility located in eastern North Carolina. Passive samplers are used to measure weekly-integrated NH3 concentrations along horizontal gradients from the lagoon/barn complex out to a distance of 500 m. Dry deposition is estimated using a canopy compensation point model. Here we present data for the period April, 2003 to August, 2005 with emphasis on modeling results and uncertainty. Dry deposition rates range from 200 kg NH3-N/ha/yr within 25 m of the lagoon/barn complex to 5 kg NH3-N/ha/yr at a distance of 500 m. Assuming a steady-state emission factor of 6.0 kg NH3/animal/yr, NH3 dry deposition over the nearest 500 m from the barn/lagoon complex accounted for 11.6 (± 3.5)% of emissions between July, 2003 and July, 2004.

Biogeochemical and Ecological Impacts and Ramifications of Atmospheric Nitrogen Deposition to Estuarine and Coastal Waters

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Abstract

Atmospheric deposition of nitrogen (AD-N) is a major contributor of externally-supplied or “new” nitrogen (N) to N-sensitive estuarine and coastal waters. Watershed N export estimates indicate that AD-N can be a significant source of N input to these waters (indirect AD-N). Direct deposition to these waters is an additionally important new N source that can bypass the terrestrial and in-stream filters that process N entering via the watershed. In European and North American coastal waters downwind of anthropogenic emission sources, AD-N contributes from 10 to over 40 percent of new N loading, and can be the single largest source of new N impacting these waters. In developing regions of the world, AD-N is one of the most rapidly expanding sources of new N. In North Carolina, USA, AD-N deposition has at least doubled since the 1970's as a result of urbanization (chiefly NOx) and more recently agricultural growth (NHX and organic N). Recent growth and intensification of animal operations in the Midwest and coastal regions (e.g., Mid-Atlantic coastal plain) have been linked to increasing amounts of NHX deposition, according to a 3 decadal analysis of the National Atmospheric Deposition Program (NADP) wet deposition network. Ammonia emitted from these operations accounts for approximately half the AD-N in nearby estuarine and Atlantic coastal waters. The ecological ramifications of this growing N source in N-sensitive estuarine and coastal waters include eutrophication, manifested as algal blooms, hypoxia and food web alterations. The role of AD-N in eutrophication dynamics depends on sources, chemical forms and amounts of N and interactions with other atmospheric nutrient sources (Fe). Trophic and biogeochemical effects of AD-N are dependent on physical conditions, including stratification, residence time, and optical properties of receiving waters. Quantitative and qualitative aspects of AD-N and other atmospheric nutrient sources may promote major biotic changes now apparent in these waters, including the proliferation of harmful algal blooms, declines in water quality and loss of fisheries habitat. Because of its relatively large contribution to total new N loading and potential biogeochemical and ecological importance in N sensitive waters, AD-N requires attention from local and regional air/watershed nutrient budgeting and management perspectives.

The Fate and Transport of Ammonia at the Local to Regional Level

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Extended Abstract

Atmospheric deposition of nitrogen (N) is a major contributor to eutrophication of estuarine and coastal waters. It is estimated to contribute 20-35% of the N load to east coast and gulf coast estuaries in the United States. Most of the N loading is contributed indirectly by first depositing on the watershed. Currently, oxidized-N from nitrogen oxide (NO_x) emissions from combustion is the major source of N in total (wet + dry) atmospheric deposition. With the anticipated control of NO_x emissions, to reduce ozone, model projections suggest that reduced-N from ammonia (NH_3) emissions will become the major source of atmospheric N deposition in the future. Agriculture is by far the largest contributor to ammonia emissions.

In some disciplinary areas the conventional wisdom is that all of the NH_3 emissions deposit locally, an idea that is not consistent with what we know in the atmospheric community.

Early budget studies with regional air quality models carried out by the first two authors suggested that at emission hot spots only a very small fraction of the ammonia emissions is dry deposited locally. Most of the emissions are lofted into the atmospheric mixed layer and transported away from the hot spot. However, the ammonia deposition velocities calculated by the regional models were very low compared to those measured in Europe. Subsequently, the deposition velocity algorithms in the Community Multiscale Air Quality model, CMAQ (Byun and Ching, 1999; Byun and Schere, 2005), were updated in 2004 with the result that the ammonia deposition velocities now calculated are much higher.

We have undertaken a new set of budget studies with version 4.5 of CMAQ at a 12-km grid size for a domain covering the eastern United States. Process analysis outputs from CMAQ, quantifying the contribution of advection, deposition and chemical processes contributing to the concentrations within a grid cell, and brute-force sensitivity analyses are used to provide the information for the budget analyses. The budget analysis has also been extended to include wet deposition as well as dry deposition and to examine the total ammonia (particulate ammonium + gaseous ammonia) budget. Total ammonia is termed NH_X. Preliminary results for June 2002 illustrate a number of findings from the fate and transport budget analysis.

At the highest emission rate cells (termed hot spots) the surface NH_X fate or budget is dominated by turbulent transport or vertical mixing. The turbulent mixing transports a majority of the surface NH_3 emissions up and away from the surface and into the atmospheric mixed layer (planetary boundary layer). Typically 2/3rds of the emissions are moved aloft. Once aloft, most of the ammonia (more than 2/3rds) is transported by horizontal advection (winds) away from the hot spot and a small fraction is converted to aerosol ammonium and an even smaller fraction is wet deposited.

Local, dry plus wet (total) deposition is an important, though not dominant, loss pathway for the ammonia emissions. With CMAQ version 4.5, approximately a quarter (15-30%) of the hot spot emissions deposit locally in the same grid cell as the emissions. The largest contributor, by far, to the local total deposition is dry deposition. For the hot spot and close-by surrounding model grid cells, dry deposition is significantly higher than wet deposition. Dry-to-wet deposition ratios for the hot spot grid cells can range from 2-10.

We also cast a wider box around the hot spots to encompass regions the size of states and larger to study the regional behavior of the ammonia budget. All of the emissions from grid cells within the box are counted in addition to the hot spot emissions. The budget is assessed throughout the vertical extent of the model which includes the mixed layer as well as the free troposphere. As the box size is increased, the emitted ammonia is increasingly converted to ammonium. At the same time, as the size of the budget domain increases, the fraction of the NH_X budget that is wet deposited increases, the fraction of the budget transported out of the domain decreases, and the fraction dry deposited rapidly stabilizes. When the box is the order of 500 km on a side then the regional ammonia emission budget tends to be divided almost equally between dry deposition, wet deposition and transport out of the region. As the domain of analysis increases further to 900-1,000 km, wet deposition becomes the major loss pathway for the regional emission budget; transport out of the domain becomes the minor loss pathway with the dry deposition fraction tending to remain about the same.

It is interesting to note that over the hot spot the NH_X dry deposition is basically all from ammonia. As the box size for the budget analysis increases, dry deposition is still dominated by deposition of ammonia gas with particulate ammonium making only a modest contribution. Over the hot spot, ammonia gas is a major contributor to the NH_X wet deposition. But as the box size increases, wet deposition is increasingly dominated by ammonium and gaseous ammonia is only a modest contributor to it.

Investigation of the magnitude of the ammonia dry deposition velocities in CMAQ suggests that they are much too high. Data from ammonia deposition field study experiments in North Carolina formed a basis for this judgment. Thus, the local budget estimates for dry deposition from CMAQ 4.5 are expected to be on the high side. To provide a more balanced assessment of the ammonia fate and transport, a sensitivity run with CMAQ has been developed in which the calculated ammonia deposition velocities are much lower, representing what is believed to be a lower bound. Ammonia emission fate and transport budget estimates will then be described in terms of an upper and lower bound from the regional air quality model analyses.

Disclaimer

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Air Quality: Policies and Standards

The Evolution of Agricultural Air Quality Regulations

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Abstract

The federal government sets health-based standards for criteria air pollutants such as ozone, PM_{10} and $PM_{2.5}$ (particles under 10 and 2.5 microns in diameter, respectively). Historically, agricultural operations have been generally exempt from air quality regulations, including permitting. That has changed dramatically in the last few years, particularly in California. This paper traces the history of agricultural criteria air pollutant regulations. The first criteria pollutant regulations on crop farms were PM_{10} dust rules, which began in the early 1990s. Regulatory programs for volatile organic compounds (VOCs) and oxides of nitrogen (NO_x), which are ozone, PM_{10} and $PM_{2.5}$ precursors, and ammonia, which is a PM_{10} and $PM_{2.5}$ precursor, are more recent.

California Senate Bill (SB) 700, adopted in September 2003, requires California air districts to adopt specific permit and other air regulations for all agricultural operations, and livestock operations in particular. This landmark legislation removed the historical exemption of agricultural operations from air permitting. California ozone non-attainment areas have been adopting regulations that require the permitting of farm equipment and amending their rules to require Best Available Retrofit Control Technology (BARCT); farms will face required upgrading or replacement of engines, gasoline tanks, and certain other equipment. Many new and modified agricultural operations will need to analyze and implement Best Available Control Technology (BACT) for equipment and, for livestock operations, farm units such as barns, corrals, and lagoons.

In addition, the U.S. Environmental Protection Agency (U.S. EPA) has issued a Consent Agreement for participating livestock farms, designed to fund a national emissions monitoring program in exchange for certain legal protections. The flood of air regulatory programs is difficult to track, but an understanding of how they evolved can give a firmer foundation for assessing their impacts on agriculture and air quality.

Introduction

The federal Clean Air Act (CAA) requires that states adopt and implement State Implementation Plans (SIPs) to achieve federal air quality standards for the criteria air pollutants, including ozone PM_{10} and $PM_{2.5}$. Until recently (circa 2003), most states exempted agricultural operations from air quality permitting. Although air quality regulations were not generally prohibited, most odor nuisance and criteria pollutant air quality regulations had exemptions for agricultural operations. This situation has changed, particularly in the West, as non-attainment regions struggle to attain air quality standards by regulatory deadlines and urban areas increasingly encroach on traditional farming areas.

PM_{10} (Dust) Regulations

The CAA requires that all serious PM_{10} non-attainment areas establish, adopt, and implement Best Available Control Measures (BACM) for all significant PM_{10} sources in those areas. The first criteria pollutant regulation on crop farms was Rule 403.1, a PM_{10} dust rule promulgated by the South Coast Air Quality Management District (SCAQMD) in January 1993 for the Coachella Valley (e.g. the greater Palm Springs desert area). Rule 403.1 was developed in consultation with Coachella Valley farmers and required the cessation of tilling during high winds, with certain exceptions. In February 1997, the SCAQMD adopted BACM amendments to its Rule 403 – Fugitive Dust, including BACM for crop farms. SCAQMD staff (including the author) worked with local farmers and farm bureaus to develop a list of agricultural dust control options, known as Best Management Practices (BMPs) for agriculture. The BMPs covered six farm areas (on-field, off-field, farm yards, track-out, unpaved farm roads and storage piles); farmers could choose from a menu of control options for each area. BMPs included high-wind tilling restrictions, mulching, windbreaks, watering/stabilizing of unpaved roads during harvest, etc.

In May 2000, Arizona adopted an Agricultural PM_{10} General Permit. The 34 BMPs that are included in this General Permit expanded on the SCAQMD BMP control options. In addition, the General Permit required at least one BMP for each of the following categories: tillage and harvest, non-cropland, and cropland. In November 2001 (Rule 8081 – off-field agricultural sources) and April 2004 (Rule 4550 – on-field agricultural sources), the San Joaquin Valley Unified Air Pollution Control District (SJVAPCD) adopted Conservation Management Practices (CMPs) for California's Central Valley, one of the most productive agricultural areas in the nation. These CMPs are more detailed than the BMPs originally adopted in other areas, and are crop-specific. Unlike other areas, farmers must submit a CMP plan for approval. A useful handbook of the CMPs and Rule 4550 requirements can be found at www.valleyair.org/farmpermits/updates/cmp_handbook.pdf. In November 2005, California's Imperial County adopted regulations similar to those adopted by SJVAPCD. Table 1 summarizes the development of agricultural BACM regulations.

Table 1. Agricultural BACM Development

Area	Rules (Adoption Dates)	BMP/CMPs	Stakeholder Group
Coachella Valley, CA (SCAQMD)	Rule 403.1 (January 1993)	High-wind tilling restriction	Local farmers and farm bureau
South Coast Air Basin, CA (SCAQMD)	Rule 403 (February 1997, December 1998)	2 to 5 BMPs for each of six farm areas	Agricultural Working Group
Maricopa County (Arizona)	General Permit – Arizona Administrative Code R18-2-610 and 611 (May 2000)	34 BMPs	Arizona Agricultural BMP Committee
San Joaquin Valley, CA	Rule 8081 (November 2001) and Rule 4550 (April 2004)	Multiple crop-specific CMPs and off-field BACM	Agricultural Technical Advisory Committee (AgTech)
Imperial County, CA	Rule 806 (November 2005)	Same as SJVAPCD rules	Technical Advisory Committee (TAC)

Ammonia (as a PM_{10} Precursor) Regulations

After leaving Los Angeles County in the 1970s due to increasing urbanization, many dairies were established in the Chino area of Southern California, just east of Los Angeles County. In its computer modeling of air pollution in the South Coast Air Basin (SCAB, i.e. the greater Los Angeles area), SCAQMD showed that as polluted air masses from the coastal counties passed over the inland dairy areas, the reaction products of the oxides of nitrogen and sulfur produced by vehicles and industries combined with the ammonia from the dairies, creating secondary aerosol particulates that contributed to peak PM_{10} levels in the SCAB. Thus, in its 1989 Air Quality Management Plan (AQMP) and every air quality plan thereafter, the SCAQMD included a control measure to reduce PM_{10} dust, ammonia, and VOCs from livestock waste (in particular, dairy manure). After working with stakeholders for more than three years, the SCAQMD adopted Rule 1127 – Emission Reductions from Livestock Waste, which established BMPs and manure disposal requirements for local dairies. The focus of Rule 1127 was on ammonia emission reductions, as part of an overall PM_{10} attainment strategy, although the rule also requires reductions in PM_{10} dust and VOCs.

At this time, the SJVAPCD is awaiting the results of the California Regional Particulate Air Quality Study (CRPAQS) before determining the role of ammonia reductions in its attainment strategy for the PM_{10} and $PM_{2.5}$ ambient air quality standards. As stated in its 2003 PM_{10} Plan: "No ammonia controls are proposed for immediate implementation in the PM_{10} Plan; however, the District is committed to pursuing an expeditious ammonia control strategy. In light of the uncertainty regarding ammonia emission controls to achieve attainment, the PM_{10} Plan includes a strategy to further assess and develop any needed control for ammonia sources, especially dairies. Implementation of any controls would depend on further analysis of the Valley's ammonia chemistry as part of CRPAQS. As the results of that study become available, the District commits to adopting ammonia control measures that have been demonstrated as technologically and economically feasible and necessary for the San Joaquin Valley."

California's Senate Bill 700 (SB 700)

In November 2001, U.S. EPA approved California's Title V program for major sources (as defined in the CAA). As in many states, California farms and farm equipment were exempt from air permitting regulations. Environmental groups sued U.S. EPA on the grounds that California's Title V program did not include agricultural sources. Under a settlement agreement, U.S. EPA issued a notice of deficiency to the state's air districts and proposed to withdraw approval of California's Title V program if the agricultural exemption was not removed. SB 700, adopted in September 2003, removed the air permitting exemption, allowing California's air districts to continue implementing their Title V programs. But SB 700 went significantly beyond simply addressing the Title V deficiency. SB 700:

1. defines "agricultural source" in state law;
2. removes the state law restriction that prohibited air districts from requiring permits for agricultural sources;
3. establishes specific permitting and exemption requirements for agricultural sources;
4. requires emission control regulations in PM_{10} non-attainment areas;
5. requires permits and emissions mitigation for "large" confined animal facilities (LCAFs); and
6. requires that the California Air Pollution Officers' Association (CAPCOA) compile a clearinghouse of information about agricultural source emission controls and mitigation strategies.

Under SB 700, air districts must require permits for all "agricultural sources" on farms with emissions of more than ½ of any Major Source Threshold for that area, unless certain findings are made at a public hearing. (For example, the Major Source Threshold for NO_x and VOC in the SCAB is 10 tons/year; in the San Joaquin Valley, it is 25 tons/year). Conversely, an air district cannot require permits for "agricultural sources" at farms with emissions less than ½ of each Major Source Threshold, unless specific findings are made at a public hearing. By definition, a livestock operation is an agricultural source, subject to permitting. The individual air districts were required to adopt or amend their BARCT rules for agricultural sources and to assess and require BACT for certain new and modified farming operations. To assist air districts in implementing SB 700, CAPCOA prepared an implementation guide, which can be found at www.capcoa.org/sb_700.htm. CAPCOA's "Agricultural Source Clearinghouse of Air Pollution Reduction Methods" can be found at www.capcoa.org/Agclearinghouse/index.html. The following sections discuss how the California Air Resources Board (CARB) and the largest air districts in California have been implementing SB 700.

California Air Resources Board (CARB)

In California, individual air districts regulate stationary sources and thus are directly responsible for adopting and implementing SB 700 regulations for farms and non-mobile farm equipment. CARB has the responsibility to set emission limits on certain off-road mobile sources found on farms and is required under SB 700 to establish the definition of an LCAF. CARB has expanded its emission inventory research for agricultural sources and has also recently expanded its guidance for the Carl Moyer Program, an incentive program that funds cleaner engines and equipment, to include a wider variety of eligible agricultural projects.

CARB conducted (and continues to conduct) several agricultural research programs. The programs include dairy and poultry emission studies (VOCs and ammonia), air quality monitoring, mitigation practice evaluations, and technology assessments. CARB is also sponsoring studies of emissions and ozone impacts of pesticides and fumigants. A summary of agriculture related research in California can be found at www.arb.ca.gov/ag/research/research.pdf. In addition, CARB hosted a San Joaquin Valley Dairy Manure Technology Feasibility Assessment Panel to help determine which technologies and management techniques are most likely to improve the management and treatment of dairy manure in the San Joaquin Valley. Panel members were drawn from government, industry, academia, and environmental and conservation groups. The final dairy manure feasibility assessment report (December 2005) and other related information can be found at www.arb.ca.gov/ag/caf/dairypnl/dairypanel.htm.

In June 2005, CARB adopted its LCAF regulation, which established LCAF permitting thresholds for all animal farms (www.arb.ca.gov/regact/lcaf05/lcaf05.htm). From the CARB LCAF staff report:

Table 2. LCAF Thresholds (Attainment status is based on the federal 1-hour ozone designation as of January 1, 2004)

Livestock Category	Nonattainment Areas*	Attainment Areas*
Dairy	1,000 milk producing cows	2,000 milk producing cows
Beef Feedlots	2,500 beef cattle	5,000 beef cattle
Other Cattle Operations	7,500 calves, heifers, or other cattle	15,000 calves, heifers, or other cattle
Chickens – Broilers	650,000	1,300,000
Chickens -- Egg Layers	650,000	1,300,000
Turkeys	100,000	200,000
Swine	3,000	6,000
Sheep and Goats	15,000	30,000
Horses	2,500	5,000
Ducks	650,000	1,300,000
Rabbits, Pheasants, Llamas, Others	30,000	60,000

For non-attainment areas, LCAF permitting rules must be adopted by June 30, 2006. Complete information on CARB's agricultural programs can be found at www.arb.ca.gov/ag/ag.htm.

San Joaquin Valley Air Pollution Control District

In May 2004, dairy groups sued the SJVAPCD over the implementation of SB 700-related permitting requirements. Dairy groups contended that under SB 700, large dairies should not be required to obtain permits until emission studies were completed. In the lawsuit settlement agreement, a Dairy Permitting Advisory Group (DPAG) was formed, with members from dairy groups, academia, and environmental groups. DPAG issues included devising a new VOC emission factor for dairies based on the most recent research, assessing BACT for dairies, and developing technical guidance on what types of dairy modifications should trigger New Source Review. DPAG submitted emission factor guidance to the SJVAPCD Executive Officer in July 2005 and made final recommendations on BACT for dairies in January 2006. More information on DPAG and DPAG projects can be found at www.valleyair.org/busind/pto/dpag/dpag_idx.htm. Although the DPAG has fulfilled its charter as laid out in the settlement agreement, many of the projects it highlighted, including emission factor research and control technology assessment, continue.

Other SB 700-related rules and rule amendments adopted by SJVAPCD include Rule 4702 (Internal Combustion Engines – Phase 2), and Rule 2250 (Stationary Equipment Registration). It also amended Rule 4202 (Cotton Gins) and Rule 8081 (Off-Field Agricultural Sources) to further reduce PM_{10} emissions and adopted Rule 4103 (Open Burning) to implement SB 705 (a law related to SB 700). The SJVAPCD is currently working with livestock industry stakeholders and the public to develop Proposed Rule (PR) 4570, which would implement the LCAF provisions of SB 700. Early discussions indicate that PR 4570 will use the CMP concept contained in SVJAPCD Rule 4550. As noted above, since the San Joaquin Valley is an ozone non-attainment area PR 4570 must be adopted by June 30, 2006.

South Coast Air Quality Management District

With the adoption of SB 700, the SCAQMD formed the SB 700 Working Group, including farm bureau and other agricultural stakeholder groups. In December 2005, the SCAQMD amended several of its Regulation II permitting rules to incorporate SB 700's definition of agricultural sources and related permitting requirements. Farmers will now have to pay permit application and annual renewal fees. In June 2005, SCAQMD amended Rule 1110.2 – Emissions From Gaseous- And Liquid-Fueled Internal Combustion Engines and Rule 461 – Gasoline Storage and Transfer to remove existing exemptions for agricultural sources. (None of the other SCAQMD Regulation XI (e.g. source-specific) rules contained exemptions for agricultural sources.) Based on these amended rules, almost all non-emergency engines greater than 50 brake-horsepower on farms will have to be replaced with electrical or controlled natural gas engines and all gasoline tanks greater than 251 gallons will require service-station-type control equipment.

As required by SB 700, SCAQMD is now imposing permit requirements on all livestock operations emitting over 5 tons/year of VOC or NO_x. With the current emission factors, this includes all dairy farms with more than 780 adult cows and all poultry operations with more than 390,000 birds. These farms may be assessed from $2,000 to over $10,000 a year in emission fees, based on current emission factors and SCAQMD regulations. All SCAQMD livestock operations, including LCAFs, are subject to the SCAQMD permitting, BARCT rules (including Rule 1127 – Emission Reductions from Livestock Operations) and BACM Rules (e.g., Rules 403 and 1186). Through the SB 700 Working Group, SCAQMD staff is working with industry stakeholders on PR 223, the SCAQMD's LCAF rule, which must be adopted by June 30, 2006.

U.S. EPA's Consent Agreement

The criteria pollutant rules and regulations discussed above are based on federal CAA requirements. As a result of court cases, livestock farms (also known as animal feeding operations, or AFOs) are also being required to comply with various other environmental laws, such as the hazardous substance release notification provisions of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, also known as "Superfund") and the emergency notification provisions of the Emergency Planning and Community Right-to-Know Act (EPCRA). Beginning in 2002, U.S. EPA worked with multiple stakeholders, including farming representatives, air agency organizations, environmental groups, and the scientific/technical community to address the issues arising from these court cases. As a result, the EPA issued its air quality Consent Agreement in the Federal Register on January 21, 2005. The consent agreement can be found at www.epa.gov/compliance/resources/agreements/caa/cafo-agr-050121.pdf. According to U.S. EPA, the goals of the Agreement are to reduce air pollution, ensure compliance with applicable CERCLA and EPCRA provisions, monitor and evaluate AFO emissions, and promote a national consensus on methodologies for estimating emissions from AFOs.

Under the agreement, livestock farms that sign the Agreement will need to pay a civil penalty ranging from $200 to $100,000 (depending on size) and provide up to $2,500 per farm location to support the EPA's data collection and emissions monitoring program. The farm must be available for emissions monitoring, apply for applicable air permits and conditions, install BACT on sources above the Major Source Threshold, and report certain releases of ammonia and hydrogen sulfide. In exchange, U.S. EPA covenants not to sue the farm for past violations of certain provisions of the CAA, CERCLA, and EPCRA, subject to certain limitations.

The sign-up period to accept the Agreement ended August 12, 2005. To date, U.S. EPA has received more than 2,600 signed Agreements, which must be ratified by the U.S. EPA's Environmental Appeals Board. Applicants are located in more than 37 states and include representation from the pork, egg layers, meat birds, and dairy industries. The monitoring program began in early 2006 and will continue for approximately 24 months. Pollutants to be monitored include particulate matter, hydrogen sulfide, VOCs, and ammonia. The latest information on the Consent Agreement program can be found at www.epa.gov/compliance/resources/agreements/caa/cafo-agr-0501.html.

Conclusions

Agricultural air quality regulations have developed rapidly from the simple dust control provisions of the early 1990s. Federal, state, and local air agencies are promulgating many different rules, regulations, programs, and policies. This brief summary of the evolution of agricultural air quality regulations is intended to provide a foundation of understanding as the science and regulation of agricultural air emissions goes forward.

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All internet references in this paper were accessed on February 14, 2005.

Agriculture and the Clean Air Act

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Abstract

This presentation will address the implications of Clean Air Act regulations and policies for farms. It will include a discussion of the potential impacts of proposed revisions of the Particulate Matter standards and the guidance and policies which will be developed to implement these standards. It will also include a discussion of the potential obligations of animal feeding operations under the Clean Air Act as well as the EPA's ongoing activities to try to look at farming operations from a cross-media perspective.

Regulating Air Pollutants Emitted by Agricultural Operations

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Abstract

We have a system of regulating emissions of air pollutants that is the envy of the world. It consists of a federal agency (USEPA) that provides the direction and over-sight for state air pollution regulatory agencies (SAPRA). The system includes federal and state rules and regulations. EPA's authority to regulate emissions of air pollutants is provided by federal law in the form of the clean air act (CAA). State's authority to regulate and enforce emission limits is derived from state laws. States usually perform the permitting and enforcement regulatory functions although USEPA periodically will take enforcement actions such as in the Buckeye Egg case. EPA provides over-sight of the state actions. States monitor and report ambient concentrations of criteria pollutants. USEPA promulgates National Ambient Air Quality Standards (NAAQS) for criteria pollutants and designates non-attainment areas. Non-attainment areas are areas where the ambient concentrations are higher than the NAAQS for a specified criteria pollutant. States develop and submit to USEPA state implementation plans (SIP) designed to bring non-attainment areas into attainment.

The goal of the system of regulating emissions of air pollutants from all sources is to protect the public. Are we regulating agricultural sources of air pollutants correctly? Some would argue that all sources of air pollutants should be regulated equally. Others would argue that rural sources of air pollutants should be treated differently. Can we ignore the location of the public? Should USEPA/SAPRA use the same emission limitations for agricultural sources located miles from the nearest occupied residence as that used for similar sources in an urban area? For example, the NAAQS for PM_{10} is $150\mu g/m^3$ (24-hour average concentration). NAAQS are most often used to determine whether areas are classified as non-attainment. USEPA and many SAPRA are limiting PM_{10} concentrations at the property line (fence line) to the NAAQS for permitting purposes. (This is a special use of the NAAQS according to an EPA representative.) The concentrations used in this "special use" of the NAAQS may be the result of modeling and/or sampling. Rural sources may be located at a considerable distance from the nearest occupied residence but because the SAPRA has used this policy for non-rural sources, this same policy must be used to regulate rural sources. Some would argue that this use of the NAAQS is inappropriate. This paper will address controversies associated with regulating emissions from agricultural operations. The topics will include (1) the proposed PM coarse (PMc) NAAQS and the proposed subtraction method for determining concentrations, (2) use of TSP (rather than PM_{10}) for requiring Title V and PSD Permits, (3) CERCLA, (4) PM_{10} and $PM_{2.5}$ sampler bias, and (5) use of dispersion modeling results for permitting and enforcement of agricultural operations.

Voluntary Versus Regulatory Agricultural Air Quality Management Policies: Proactive Is Better Than Reactive

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Abstract

As the stewards of more than half the US land mass, those engaged in agriculture are key to the future success of incentive based environmental management. Farmers and producers should realize though that the best time to act to develop voluntary approaches to problem resolution is before regulatory actions are in the wings. When regulatory programs are inevitable, it is in the interest of agricultural get to the table early to make sure the programs are effective both economically and technically.

Discussion

Frequently cast as the first environmentalists, most farmers and livestock producers would readily take the actions needed to reduce their environmental footprint if it could be done in an economical way. Unfortunately, controlling losses to the environment typically costs more than when such control costs are externalized. How then can the problems of agricultural atmospheric emissions be controlled without giving away the farm? The answer may be that agriculture needs to take proactive steps to embrace new approaches and new allies. For example, traditionally, the federal Farm Bill has contributed money to help farmers achieve price stability for crops and, to a lesser extent, to help pay for actions on the farm which lead to improved environmental performance. However, in current international debates, trading concerns over Farm Bill crop subsidies are increasingly a problem. A proactive approach for the agricultural industry to simultaneously resolve this problem as well as many of its environmental concerns might be to join with the broad coalition of groups supporting the restructuring the Farm Bill towards increased funding for conservation practices and habitat protection.

In addition, the agricultural industry will likely be more successful in getting voluntary incentive based control programs if its members step up to the plate in other areas before regulatory actions are looming. A prime example of such an opportunity currently exists for green house gases. For example, a voluntary green house gas registry and a transferable credit system has been recommended to President Bush by the Secretaries of Energy, Commerce, and Agriculture and the Administrator of EPA. Even though agriculture's role in green house gas emission reductions are solely as a sink, fear of potential mandatory reductions if any green house gas emissions are acknowledged seem to be paralyzing many in the agricultural industry. Might mandatory reductions of green house gases fall upon agricultural activities in the future? Yes, but an effective program with farmers providing carbon credits would not speed such regulations and the experience gained will serve farmers well if regulations do come about.

It is understandable that agriculture also wants certainty in existing regulatory programs. Efforts such as the EPA AFO Consent Agreement and Final Order are driven by those desires for certainty. But such efforts must be developed in an open forum, and be adequate to achieve their goals if they are to have wider support. Furthermore, frustration from all interested parties over the air emissions regulatory programs such as CERCLA have led to a very nonproductive situation. Eventually, emissions of gases such as ammonia from agricultural activities will need to be directly addressed. If new regulations mandate controls, will they be misguided and inappropriate for agriculture? Chances are much greater that they will be unless representatives from the agricultural industry are at the table working to create control programs that make sense for farmers and are effective in controlling emissions.

Implications of PM Coarse Federal Air Quality Standard for Agriculture

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Abstract

The EPA is proposing a revised particulate matter (PM) national ambient air quality standard (NAAQS), which establishes a dual standard that parses the current PM_{10} standard into fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) fractions. In arid western regions of the U.S., multiple factors converge causing emissions and transport of airborne PM from cultivated agricultural fields that have caused numerous exceedances and violations of the PM_{10} standard. Violations of the NAAQS can lead to EPA sanctions and extensive planning efforts associated with declared non-attainment status. The proposed $PM_{10-2.5}$ NAAQS lowers the bar for exceedances and violations with a proposed level of 70 $\mu g{\bullet}m^{-3}$. Implicit in this level is the assumption that the $PM_{2.5}$ to PM_{10} ratio is approximately 0.50. However, this ratio is not independent of total concentration ($\mu g{\bullet}m^{-3}$) of PM in the airborne dust, the mechanism of entrainment, or source characteristics. Data for the arid region of the Columbia River Plateau in eastern Washington State shows that during a wind erosion event the $PM_{2.5}$ to PM_{10} ratio tends to decrease (approaching 0.04) as PM_{10} concentration increases. This variance of the ratio coupled with the reduced concentration threshold of the $PM_{10-2.5}$ standard indicates a significant probability that exceedances and violations of the federal standard will increase from 4- to 15-fold, which falsely gives the appearance of serious air quality deterioration.

The EPA's Natural Events Policy (NEP) issued in 1996 addresses violations of the federal PM_{10} standard from high wind soil erosion events, which are generally beyond reasonable management control. The latter includes cultivated agricultural fields that have best management practices (BMP) or best available control measures (BACM) in place but are overwhelmed by wind erosion events. The NEP calls for documentation of a natural event to characterize an exceedance that occurred as a consequence of overwhelmed BACM. Acceptable documentation means that such exceedances can be excluded from counting toward a violation. Adverse consequences and significantly more complications in implementation of the NEP may result as the $PM_{10-2.5}$ standard increases the frequency of exceedances by several-fold. As the number of exceedances significantly increases, so does both the documentation workload and burden of proof as a natural event. These factors coupled with a perceived worsening of the problem may decrease EPA's regulatory tolerance beyond that which can be addressed with the Natural Events Policy. Many questions arise from the $PM_{10-2.5}$ NAAQS proposal.

Introduction

The geological history of the area includes catastrophic flooding from build up of water behind ice dams during the ice age, which subsequently were catastrophically breached. The ensuing floods sent several hundred feet of water carrying massive amounts of sediment that was deposited in various areas across the Columbia River Plateau. The soils that we have today are a result of subsequent re-working and re-depositing by water and wind. The soil texture is dominated by silt and sand-sized particles with low clay and organic matter content, which causes inherently low aggregate stability. These soils are inherently vulnerable to wind erosion. The immediate aftermath of catastrophic floods was massive aeolian or windblown sediment transport (major dust storms) amounting to many tens of feet of deposition downwind from the flood deposits.

The general precipitation level varies from approximately 5 inches to 25 inches across the Columbia Plateau with the most vulnerable areas to wind erosion in the lower precipitation areas. Natural vegetation of shrub-steppe eventually stabilized the landscape but frequent natural fires made the landscape vulnerable to dust storm conditions without significant anthropogenic influence. Every era of history after the flooding saw dust storm events in which overall landscape stability varied with weather and climate patterns, which in turn further interacted with landscape stability to produce windblown dust events.

Anthropogenic factors were active even in early native settlement. The low native population generally produced only a low degree of anthropogenic disturbance but included area burning deliberately set for various cultural reasons. Subsequent settlement brought ranching and crop production and increasing population with associated increase in landscape disturbance and perturbation. Consequently the probability increased for wind events that produced dust storms. Dryland and irrigated cropping have become a significant percentage of land use complimented by rangeland, nearly native areas, and some largely undisturbed native areas. Land uses in this region of Eastern Washington include native shrub steppe, rangelands, dryland agriculture, and irrigated agriculture. Today small urban areas with cities of substantial population density also exist as a land use within the Columbia Plateau.

Modern management practices on cropland with the goal of maintaining vegetative cover on the soil surface have been developed and annual landscape stability is relatively good. However, there are a few windows of vulnerability that occasionally correspond to wind events capable of producing dust storms. These dust storms impact people in the urban areas.

Discussion

History of Windblown Dust Exceedances of PM_{10} NAAQS

Ambient air quality in Kennewick Washington, located in the southwestern portion of Columbia Plateau, is measured and represented by a PM_{10} federal reference method (FRM) monitor. Another PM_{10} FRM site is located approximately 135 miles to the northeast in Spokane Washington. Both these FRM sites have recorded numerous windblown dust exceedances of the PM_{10} national ambient air quality standard (NAAQS) since this standard was established in 1987. Both Kennewick and Spokane are small urban areas and are located downwind from several thousand acres of non-irrigated and irrigated agricultural fields. The airborne PM measured at the air quality monitoring sites comes principally from a combination of wind erosion from upwind agricultural fields and active construction sites in the urban area. Other sources such as re-entrained paved road dust, unpaved roads, and dust from other dust-generating sources also contribute.

In addition to its downwind location, Kennewick is generally vulnerable to windblown dust for a number of reasons, including an arid climate, soils with inherently high potential for wind erosion, periods of low overall landscape stability, and a sufficient frequency of high winds to drive severe wind erosion. Figure 1 shows the exceedances from agricultural windblown dust measured from 1985 through 2005 at Kennewick. The long-term frequency of PM_{10} NAAQS exceedances at Kennewick is approximately one every 7 months (37 exceedances in 20 years). The PM_{10} NAAQS form in 40 CFR Part 50 Appendix K allows only 1 exceedance per year and the frequency of observed exceedances causes the Kennewick area to be in violation of the NAAQS.

The distribution of exceedances in time varies with weather patterns such as periodic droughty conditions. Figure 2 shows the distribution of exceedances among months in which they occurred as well as the relationship to the annual precipitation pattern. Based on analysis of historical weather data an aridity or drought index, which combines temperature and precipitation data, shows a periodicity of roughly 10 to 12 years (data not shown). Twenty years of PM_{10} FRM monitoring at the Kennewick site reflects this in the periodicity of PM_{10} NAAQS exceedances (Figure 1) and very roughly confirms this observation.

Addressing Windblown Dust since PM_{10} NAAQS was Promulgated

The Columbia River Plateau is centered in Eastern Washington and extends into western Idaho and northeastern Oregon. Several other FRM monitoring sites are located in the Columbia Plateau region and also frequently record PM_{10} NAAQS exceedances. Many of these exceedances happen on the same dates region-wide across the Columbia Plateau. The coincidence of these exceedances is indicative of large region-wide wind events and corresponding dust storms. The passage of weather fronts on a regional scale drives strong gusty winds and causes the windblown dust events that, given unstable landscape conditions, result in PM_{10} NAAQS exceedances. The peaks in March and September (See Figure 1) are associated with agricultural tillage and planting operations that coincide with winter-spring and summer-fall weather transition periods that are characterized by front passages with attendant high wind speeds and gustiness.

Figure 1

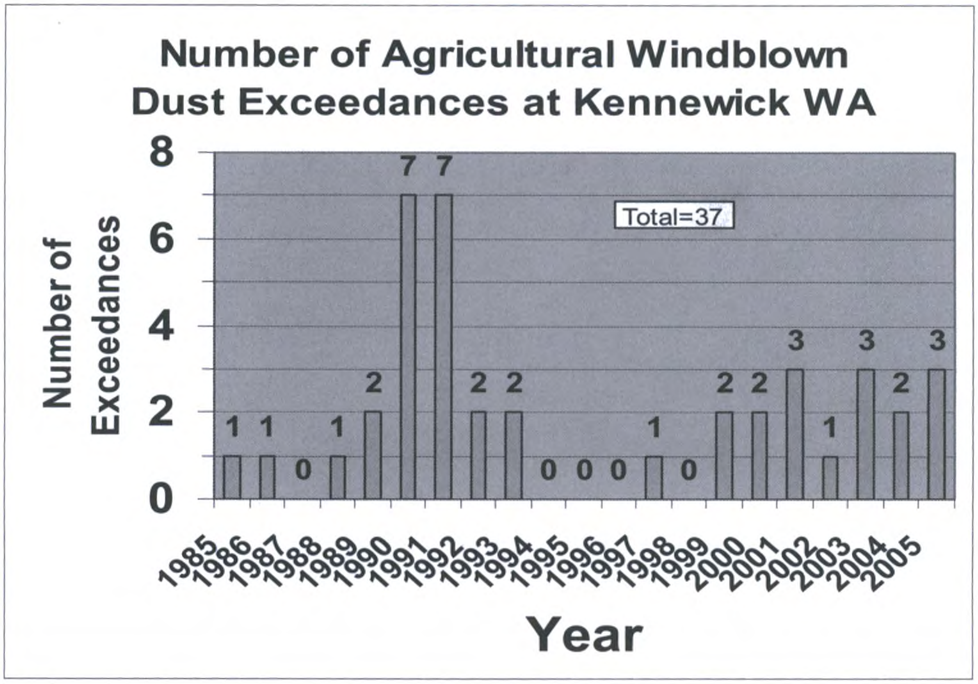
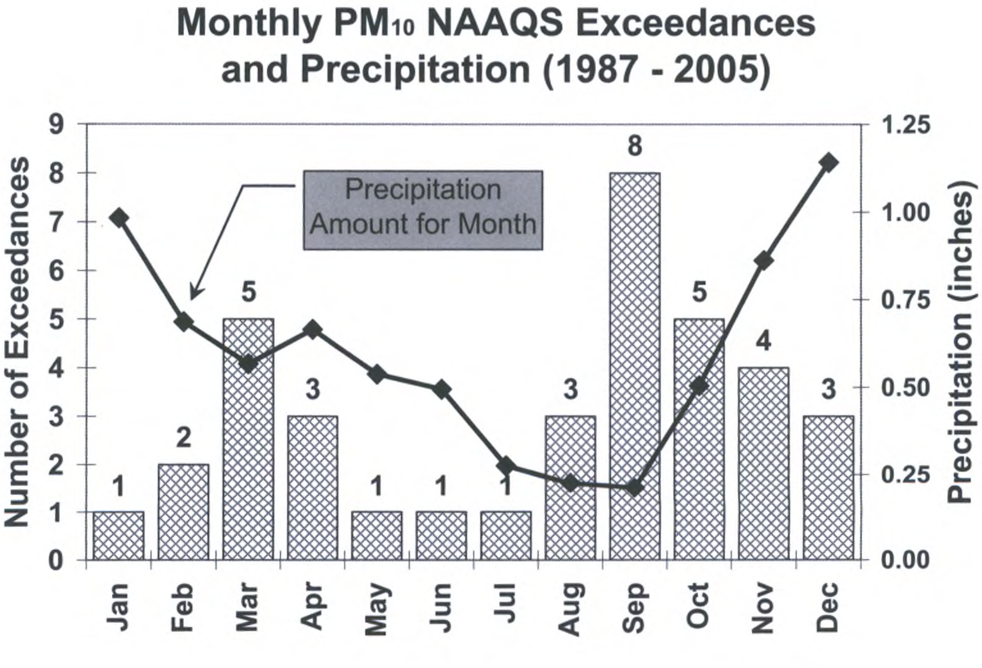


Figure 2



To address the PM_{10} NAAQS exceedances at Kennewick through 1993 a Memorandum of Agreement (MOA) was used as precursor to the current EPA Natural Events Policy (NEP) for windblown dust, which allows PM_{10} NAAQS exceedances to be discounted from contributing to a NAAQS violation. The period before the 1996 adoption of the NEP was covered by the MOA among the Benton Clean Air Authority (BCAA), Washington State Department of Ecology (Ecology), and the EPA. All parties mutually agreed that major wind events could overwhelm even best management practices. Therefore, the traditional non-attainment procedures would not correctly target or bring about demonstrable control of windblown dust. From 1996 forward, the requirements of the NEP have been implemented by the BCAA and Ecology to deal with windblown dust PM_{10} NAAQS exceedances. To date in Eastern Washington Natural Events Policy documentation has been used to exclude 15 PM_{10} NAAQS exceedances from counting toward a violation of the standard.

Transition from PM_{10} to the Proposed $PM_{10-2.5}$ NAAQS

After the promulgation of the 1997 $PM_{2.5}$ NAAQS, both the $PM_{2.5}$ NAAQS and the PM_{10} NAAQS have been under intense scrutiny by stakeholders on both sides of the issue. The result has been a parsing of the original PM_{10} fraction into "fine" ($PM_{2.5}$) and "coarse" ($PM_{10-2.5}$) fractions. The basis for this division is the fundamentally different physical and chemical makeup of the two fractions. The fine fraction, $PM_{2.5}$, originates predominately from combustive processes plus formation of aerosols of inorganic salts such as ammonium nitrate, sulfate, and chloride. The coarse fraction, $PM_{10-2.5}$, is of different origin coming principally from such sources as windblown dust generated from the mechanical disturbance of soils and mining activities, which frequently involves crushing of rock and other activities that generate dust. The majority of $PM_{10-2.5}$ consists of crustal material or minerals found in rock and soil.

Previous to the announcement setting the proposed level, analysis of the frequency of exceedances of a range of estimated $PM_{10-2.5}$ concentrations revealed that when the ratio of $PM_{2.5}$ to PM_{10} is low the number of $PM_{10-2.5}$ exceedances would be several-fold that observed for current PM_{10} NAAQS (See Table 1). That is, a low $PM_{2.5}$ to PM_{10} ratio in effect makes $PM_{10-2.5}$ concentration nearly equivalent to PM_{10} concentration, which then naturally would more frequently exceed the lower threshold (below 150 $\mu g{\bullet}m^{-3}$) concentration for exceedances in proposed $PM_{10-2.5}$ NAAQS.

Table 1: Estimated Increase in Number of NAAQS Exceedances at Various Threshold Levels of the Proposed $PM_{10-2.5}$ Standard

Selected $PM_{10-2.5}$ Daily NAAQS Value	Estimated $PM_{10-2.5}$ Exceedances (1999 – 2002)	Observed PM_{10} Exceedances (1999-2002)	Estimated Increase (fold)
75	29	8	3.6
65	36	8	4.5
55	48	8	6.0
45	71	8	8.9
35	120	8	15.0

When the details of the new proposed PM national ambient air quality standard (NAAQS) were revealed on 20 December 2005 it perhaps raised more questions than it answered regarding implications of the standard for areas where windblown dust is significant or even the sole contributor to the monitored PM levels. The proposed $PM_{10-2.5}$ concentration level is 70 $\mu g{\bullet}m^{-3}$. Frequency analysis was preformed on 20 years of PM_{10} data collected at Kennewick from 1985 through 2005. In this period there were 37 exceedances of the PM_{10} NAAQS at 150 $\mu g{\bullet}m^{-3}$. Estimated $PM_{10-2.5}$ concentrations were calculated from a $PM_{10-2.5}$ to PM_{10} ratio of 0.96. The latter ratio was determined from asymptote and linear regression analyses from x-y plots of PM_{10} concentration against $PM_{2.5}$ to PM_{10} ratios and $PM_{10-2.5}$ concentrations, respectively (See Figures 3 and 4). The ratio estimate is valid only at PM_{10} concentrations above 70 $\mu g{\bullet}m^{-3}$

Figure 3

PM_{10} Concn µg/m³	$PM_{2.5}/PM_{10}$ Ratio Mean	Std Dev	N	Coefficient of Variation
>=75	0.062	0.035	34	56%
<75	0.36	0.22	1220	62%

PM_{10} Concn µg/m³	$PM_{2.5}/PM_{10}$ Ratio Mean	Std Dev	N	Coefficient of Variation
>=37	0.19	0.17	182	89%
<37	0.37	0.22	1072	58%

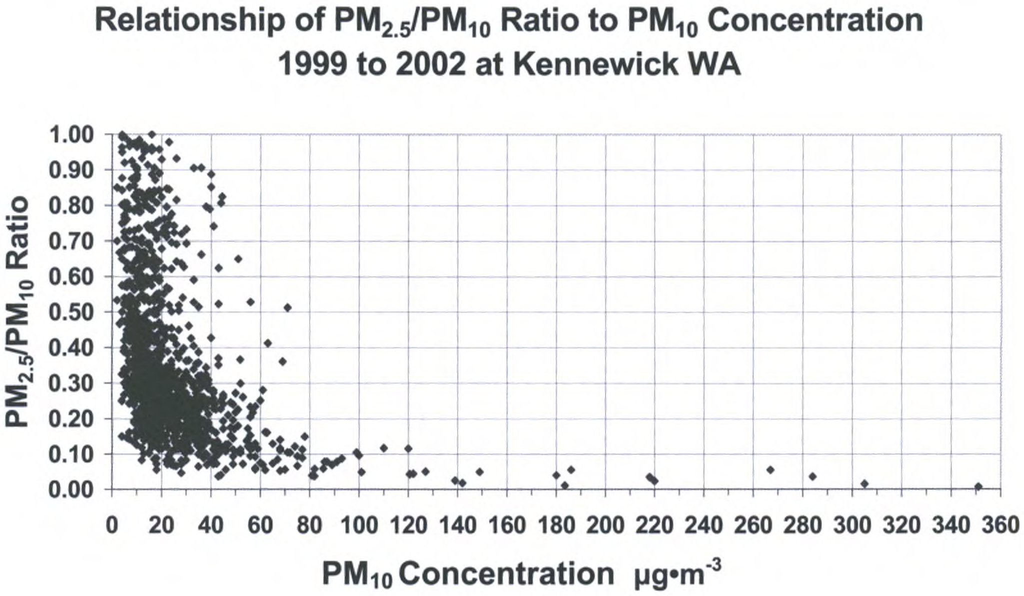
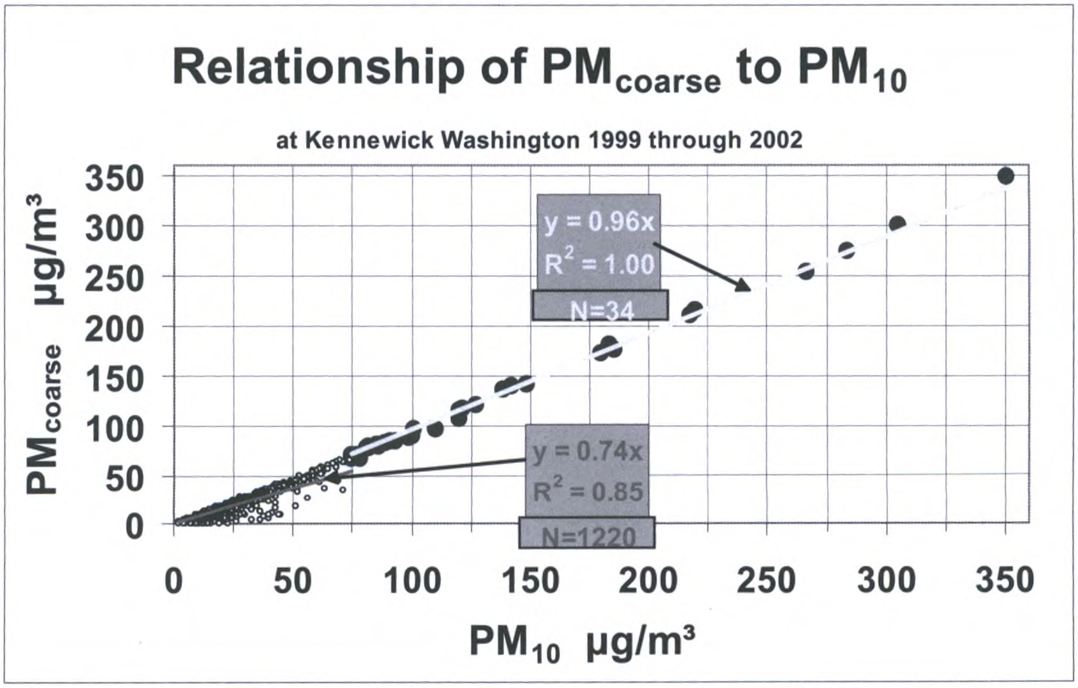

Relationship of $PM_{2.5}/PM_{10}$ Ratio to PM_{10} Concentration 1999 to 2002 at Kennewick WA

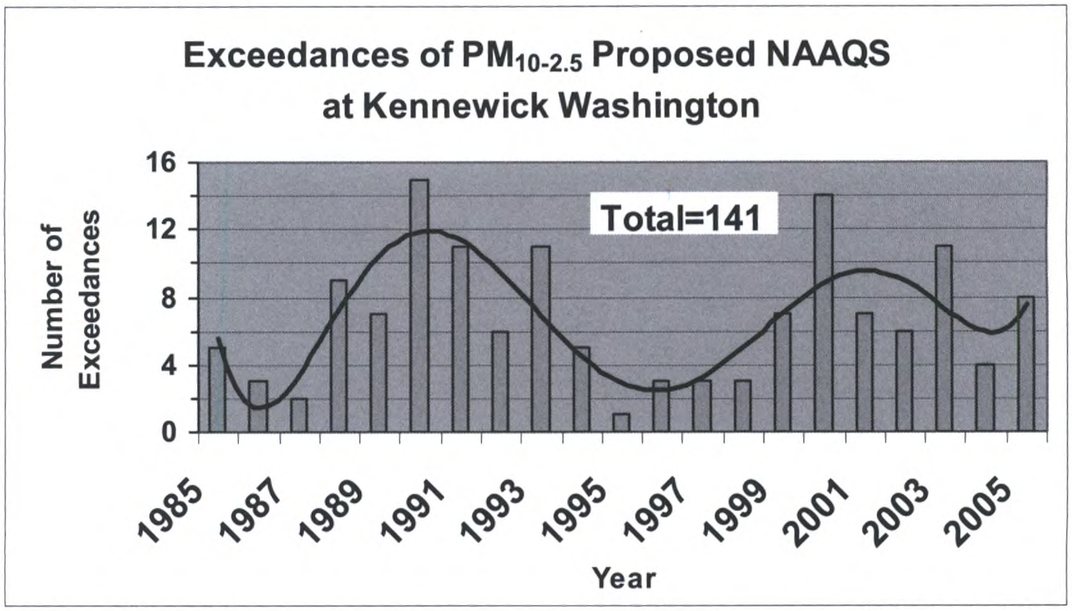
Figure 4


Relationship of PM_{coarse} to PM_{10}

at Kennewick Washington 1999 through 2002

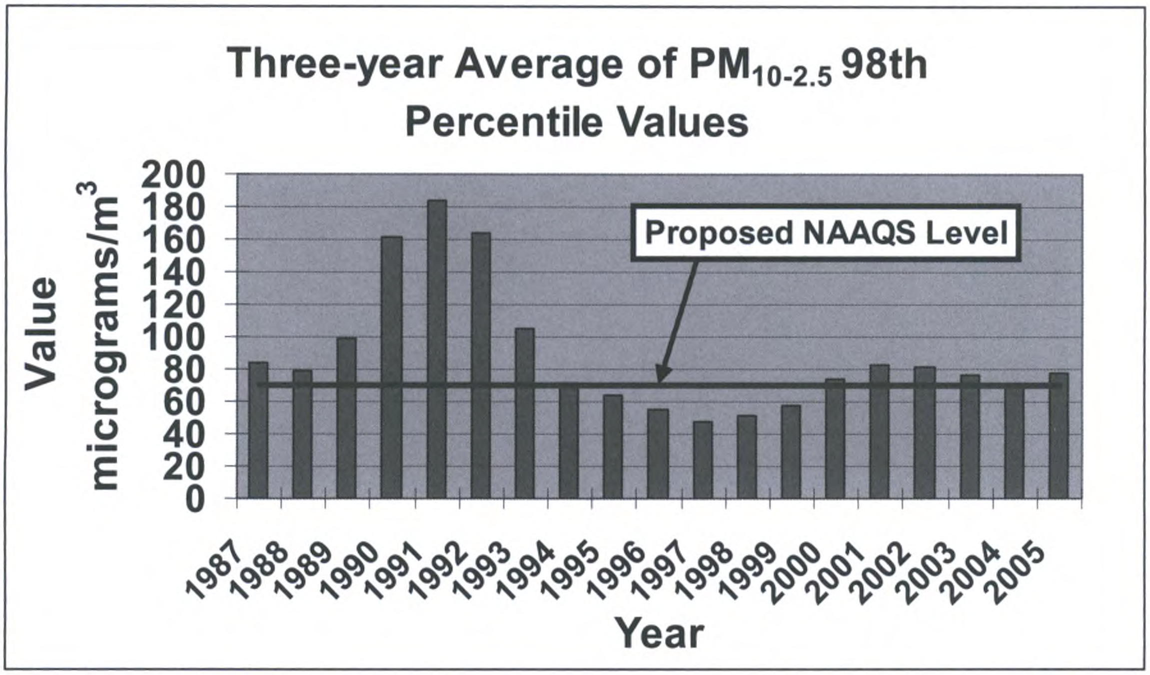
The calculated $PM_{10-2.5}$ values exceeded the proposed level of 70 µg•m^{-3} a total of 141 times from 1985 through 2005, which is 3.8 times the number of recorded PM_{10} exceedances (See Figure 5).

Figure 5



The form of the daily (24-hour average) for $PM_{10-2.5}$ NAAQS is the three-year average of 98th percentile values compiled and calculated annually. If the proposed $PM_{10-2.5}$ NAAQS is implemented in the latter form the Kennewick area could nearly be in perpetual violation of the standard. Figure 6 shows the years in which $PM_{10-2.5}$ NAAQS violations (as opposed to exceedances) would have occurred in the period of 1987 through 2005. Each value in a particular year is the average of the 98th percentile value for that year and the previous two years. The larger peak in 1991 occurred when prolonged drought and winter-kill of dryland wheat in the agricultural fields upwind of the Kennewick monitor progressively depleted crop residues at the soil surface until the stability of the landscape decreased to a point that it was extremely vulnerable to wind erosion. The resulting estimated $PM_{10-2.5}$ exceedances would have kept the area in violation of the NAAQS from 1987 through 1994. Normal to above average precipitation that actually began in 1992 and continued through 1998 caused the violations to cease in the period 1995 through 1999. Another period of deficit precipitation began in 1997 and continued through 2005 and predictably $PM_{10-2.5}$ NAAQS violations again resumed from 2000 through 2005. Note that the occurrence of violations reflects several years of lag time of the effects of the droughty periods that are associated with the time required to deplete or build up crop residue. This is a result of the 2-year summer fallow winter wheat growth cycle that dominates the agricultural fields upwind from the Kennewick monitoring site.

Figure 6



Implications of the Proposed $PM_{10\text{-}2.5}$ for Agriculture

The only thing that is certain about the situation regarding implications for agriculture from the proposed $PM_{10\text{-}2.5}$ NAAQS is uncertainty. The complicating aspect of the proposed $PM_{10\text{-}2.5}$ NAAQS with respect to agriculture is the unprecedented categorical exemption from the standard that is a proposal to exclude windblown dust from agricultural fields. Dust from mining activity was also included in this exemption. At first it appears that there are no implications to agriculture because of the categorical exemption. However, depending on the view taken, this exemption could be a desirable outcome or a snake in the grass some time in the future. This is the first time that a NAAQS has been proposed that did not apply nationwide. The origin of this exemption is apparently principally because of lack of evidence for significant health effects and mortality associated with exposure to the coarse fraction of inhaled $PM_{10\text{-}2.5}$. One possible problem with this approach is that lack of epidemiological evidence does not necessarily mean no health effects exist, but presently there is simply not sufficient statistical power to detect the effects because of lack of a sufficient population in the sample. What will be the position of EPA if at some future time health effects are found to be significant from exposure to agricultural windblown dust?

There is also the potential loss of credibility from suddenly abandoning the long standing PM_{10} standard that for 20 years has been a concern and attributing any health effects only to the embedded $PM_{2.5}$ fraction. The implicit assumption in the current proposal is that rurally-derived $PM_{10\text{-}2.5}$ is pristine and only urban-derived dust is contaminated with harmful components. There are pesticides, some of which are classified as toxic, persistent, and bio-accumulative, that may be associated with rural dust and may be adsorbed to the particles and carried along to distant receptors. Soils in fields adjacent to heavily traveled paved roads through rural areas may have accumulation of lead carried over from the use of lead additives in the past. There may also be some as yet undetected direct effect from the physical and chemical interaction of coarse particles within the respiratory system.

There is also what is known as "welfare" effects of ambient air quality standards, which are deleterious effects other than health effects. Visibility is one of these effects, which includes degradation of long-distance visibility of desirable vistas. Also there is degradation of short-distance visibility adjacent to agricultural fields that obscures roadways and causes safety hazards to traffic and road closures. Deposits of dust on public and private property, into adjacent bodies of water, on sensitive equipment are other examples of welfare effects. These are all effects that can be a result of windblown dust from agricultural fields that can be close to the source or hundreds of miles away as even $PM_{10\text{-}2.5}$ can be entrained and remain airborne for many hours to days.

There is a momentum and forward movement in rural areas to take responsibility for wind erosion and resulting long-distance transport of coarse fraction PM. Resources have been and are being allocated to conservation of soil and water resources related to wind erosion and windblown PM. The EPA agricultural exemption in the proposed $PM_{10\text{-}2.5}$ NAAQS takes away some of the incentives to pursue these efforts and continue development of good management practices for wind erosion control. Similarly, if global scale and international transport of PM from overseas dust storms, which is coming from unprotected rural landscapes in other countries, proves to be a significant contributor to air pollution in the U. S. then this categorical exemption of agricultural sources here may adversely affect getting cooperation to mitigate these remote sources.

There may also be other factors because the swarms of expected exceedances at monitoring sites in areas such as Kennewick would overwhelm the current Natural Events Policy (NEP). Multiple NEP documentation submissions would result. For Kennewick these exceedances and NEP documentations would be clustered in March and September but the lower concentration threshold for NAAQS exceedances will also increase the number observed at other times of the year. Estimated frequency on average could approach once per month. Of course, the exemption of windblown dust from applicability of the proposed $PM_{10\text{-}2.5}$ NAAQS would eliminate having to deal with the current NEP requirements for windblown dust.

In addition to the NAAQS itself, there are two other aspects of the revised NAAQS package, which are a revised ambient air monitoring strategy and a proposed overhaul of the exceptional event and natural events policies that will be captured in rule form. An exceptional and natural events rule will cast the approach to these situations in concrete. As of this writing the proposed monitoring rule is published and the exceptional/natural events rule is pending. Therefore, how this pending rule will interact with the NAAQS and monitoring pieces cannot be evaluated.

The intent of the monitoring strategy for $PM_{10\text{-}2.5}$ is to concentrate the effort on urban-generated particles that will capture dust from construction sites, re-entrained from paved roads, and any direct emissions of $PM_{10\text{-}2.5}$ from industrial sources. There are five criteria for siting of FRM monitors for $PM_{10\text{-}2.5}$ as are follows:

1) The site must be in a U.S. Census Bureau-defined urbanized area that has a population of at least 100,000 people, which is intended to measure an ambient mixture of $PM_{10\text{-}2.5}$ dominated by PM generated from re-suspended road dust from high-density traffic on paved roads, industrial sources, and construction sources.
2) The site must meet a minimum density threshold of 500 persons per square mile for the Census block group containing the monitor, which is intended to minimize the ambient impact from rural dust, agriculture, or mining.
3) The monitor must be population oriented, which is intended to locate sites in residential areas, recreational areas, industrial areas, or other areas where a substantial number of people may spend a significant fraction of their day.
4) A monitoring site must not be adjacent to a large emissions source or in an area affected by a large source, which would make the $PM_{10\text{-}2.5}$ NAAQS more community-oriented with the appropriate degree of stringency. EPA intends the $PM_{10\text{-}2.5}$ NAAQS to have the same stringency as the current PM_{10} NAAQS, which is reflected in the fact that all or most of the current PM_{10} monitoring sites are not adjacent to large emission sources.
5) A site-specific assessment must show that the ambient mix of $PM_{10\text{-}2.5}$ would be dominated by PM generated from re-suspended dust from high-density traffic on paved roads, industrial sources, and construction sources. The intention is also that ambient mix at the monitoring site would <u>not</u> be dominated by PM generated from rural windblown dust and soils, other agricultural sources, or mining sources.

These criteria are problematic for the Kennewick monitoring site because, while it meets some of these requirements, avoiding impact from agricultural dust is not possible. The major source of windblown dust at Kennewick is directly upwind of the urban area and no place could be found that simultaneously satisfies all of these criteria. Despite not meeting all these criteria, it is likely that an urban area the size of

Kennewick including the near-by cities of Richland, Pasco, and West Richland will qualify for official federally approved and certified monitoring for purposes of compliance with of the $PM_{10-2.5}$ NAAQS. In the foreseeable future, the combined population of this quad-cities area will approach 250,000. Furthermore, there are even smaller urban areas in the arid western region of the country that are heavily impacted by airborne PM. This brings up environmental justice issues with regard to whether people in these smaller urban need protection of their ambient air.

A corollary problem for the Kennewick monitor results from the probable inability to meet the criterion of avoiding the influence of rural windblown dust while simultaneously capturing the construction and other urban dust sources. Separating or allocating the measured dust from these multiple sources and deducting the overwhelmingly large component coming from the windblown agricultural dust presents a challenging technical problem. It is not at all clear if such methodology exists and if it does exist is it economically and technically feasible to use it?

The emphasis on the concept that agricultural $PM_{10-2.5}$ is solely associated with dust emitted from agricultural fields also potentially ignores the fact that there is also this size fraction in smoke from vegetative burning. The many potential harmful compounds that are products of combustion vegetation as well as the fundamentally different composition of PM from combustion raises more questions about a blanket exemption of $PM_{10-2.5}$ from agricultural sources that characterizes this PM as only from crustal sources. Agricultural burning could also be a source of $PM_{10-2.5}$?

Other locations in the arid west may have situations similar to that described in this paper but attempting to address other areas was beyond the scope of this paper. This paper should be considered as a case study and hopefully there are some lessons, commonalities, and principles that could be applicable in similar situations. The uncertainty leads to many questions.

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Biomass: Burning, Decomposition

Considerations for Biomass Burning in Wildlands and Agriculture

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Abstract

The need for managing smoke resulting from wildfire and other forms of biomass burning is increasing. Management of smoke is a steadily maturing activity in the United States which has been built upon a foundation of many years of needs assessment. This maturation is driven by both a desire on the part of wildland fire managers to do the right thing and the increasing likelihood of regulatory attention. Regulatory interest in biomass emissions is driven by regional haze regulations and the possibility of new national ambient air quality standards (NAAQS) for particulate matter, with standards for particles smaller than 2.5 microns (PM2.5) and between 2.5 and 10 microns (PM10-2.5) as prime examples. Five years ago an assessment of tools needed to support technical smoke management was completed under the US Joint Fire Science Program. Recommendations included new research and development initiatives for tools in three categories. These categories were wildland fire 1) strategic and tactical planning, 2) operations, and 3) post-fire evaluation. This paper reviews what has been accomplished during the last five years, and in so doing, identification is made of some continuing research needs and remaining challenges. The application of what we have learned about wildland fire emissions and management of smoke has both implication and utility for agriculture. In conclusion, this paper will discuss how biomass burning for agriculture may both converge and diverge from forestry and rangeland applications, with some practical suggestions made for next steps.

Global Scale Analysis of the Atmospheric Impact of Fire Emissions

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Abstract

Biomass fires associated with human activities such as forest and savanna burning for agricultural and other purposes, burning of agricultural residues, and domestic burning of biofuels, represent a significant source of chemically and radiatively important trace gases and aerosols to the atmosphere. Over the last two decades, there has been considerable progress in quantifying the spatiotemporal distribution of fire emissions, and in understanding their impact on atmospheric chemical composition. In this paper, we review our current knowledge in this area, focusing in particular on recent large-scale fire emission estimates derived using multiple satellite products in a modeling framework involving biogeochemical and atmospheric chemistry models. One focus of our analysis will be on assessing the consistency of the satellite-derived fire emissions with independent estimates in regions where agricultural open field burning occurs. A second focus of analysis will be on delineating the potential impact of emissions from large-scale fires on air quality in various agroecological zones.

An Air Quality Impacts Planning Tool

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Introduction

Newly revised clean air standards and new regional haze rules are prompting emitters and regulators (states, tribes, and county or local air agencies) to develop more accurate accounting of emissions and impacts. At the same time, there is an increasing use of fire in forested landscapes to help reduce hazardous fuel buildup and maintain and restore healthy ecosystems. The result is that in many parts of the country, agriculture and forest activities are directly competing for the same air space.

There are few tools that allow forest and agricultural land managers to understand the likely air quality impacts, or even regions impacted, by their controlled burning practices. Ferguson (2001) recently compiled a summary of tools available for managing smoke from wildland fire and found that most tools are too simple to be realistic or too complicated to be employed regularly. The result is inconsistent assessment of smoke impacts, inconsistent or unreasonable regulation, and little if any information on alternative scenarios that could allow burning to continue with reduced impact.

Currently, there is no way of rapidly assessing impacts from new sources or of understanding the cumulative impact from multiple sources. This is particularly critical for temporary sources such as planned agricultural burns and prescribed fire treatments. Because there is no way of rapidly assessing the impacts from these sources, there is no easy way to experiment with alternatives in location or timing of a source that could help mitigate impact. Thus agriculture and forest managers and air regulators cannot game play and negotiate to help maintain air quality.

To fill this need, we are creating a new web-based tool for helping to anticipate air quality impacts from point sources, which we have called the Air Quality Impacts Planning Tool (AQUIPT, http://www.airfire.org/aquipt). By combining the power of air quality dispersion models with historical weather information over a long period of time, AQUIPT allows users to determine likely emissions impacts beyond the 5 day forecast limit of dynamical weather models.

While it cannot answer what the impacts will be in the future, say this September, by utilizing 30 years of historical data, AQUIPT shows probabilistically what the impacts would have been based on the previous 30 Septembers. In this way, AQUIPT attempts to fill a needed gap in a suite of tools available to agricultural, forest, and air regulator users.

Methodology

AQUIPT has been developed from the BlueSky smoke modeling framework (O'Neill et al., 2005), although significant alterations have been made to BlueSky for this purpose. While the BlueSky framework was originally designed for use with short term weather forecasts, AQUIPT relies on a longer term (30 year) database of hourly historical weather.

Via a website, users submit requests for analysis of a point source of interest. The user can specify the type of point source: wildfire, prescribed burn, agricultural burn, factory, dairy farm, among others. The user can choose from default parameters for the source, or supply known information. The user can supply a particular period of interest (for example specific calendar months).

After submission of the request, the model is run on a cluster computer. In order to generate the requested results, multiple model runs are performed and statistically aggregated. The emissions source is run for a 3 day period starting every day of the selected time period over the past 30 years. For example, if the user requested information for September impacts, 30 days*30 years = 900 3-day model runs are performed.

Statistical aggregates of the output are collected and mapped. The user is then notified that the results are available via email, and they can view and download the maps on the website.

Historical weather information is needed as hourly three dimensional gridded fields at 36-km horizontal resolution for the full 30 year time period. This requires a very large (multi-TB) database. This database is created by downscaling historical climate observations using a mesoscale meteorological model. Global climate model renanalysis products have been created that incorporate historical observations and therefore represent a "best-guess" at the state of the atmosphere; we utilize the National Center for Environmental Prediction/National Center for Atmospheric Research reanalysis product for the period 1970-2000. We are also investigating using the European Center for Medium Range Forecasting (ECMWF) reanalysis product. These products need to be downscaled for our purposes. Downscaling is done with the NCAR/Penn State MM5 mesoscale model in a nested mode down to a 36-km grid over the contiguous 48 states. During downscaling four dimensional data assimilation (FDDA) is utilized to nudge the model with observations. The meteorological data is run through the CALMET model for use by the CALPUFF dispersion model.

Emissions are generated utilizing standard profiles for various types of point sources. For wildland fires, emissions are calculated from regional fuel loadings and the CONSUME/EPM emissions model. Other types of sources have proscribed emissions profiles and speciation that is scaled by the user specified size of the source.

Dispersion/transport is done by the CALPUFF dispersion model. CALPUFF is a standard puff type model. Output from the dispersion model is aggregated utilizing specialized code and then statistical maps are generated by the FERRET visualization tool.

Status and Summary

The AQUIPT project is currently in its second year of development. A prototype tool is functional for testing purposes.

The largest portion of work has been the development of the historical climate database. As we require full 3-dimensional fields for the dispersion/transport modeling, this database must be generated by downscaling from global climate model reanalysis products. We are currently utilizing the National Center for Atmospheric Research (NCAR)/National Center for Environmental Protection (NCEP) reanalysis product, but we are also investigating switching to the European Center for Medium Range Weather Forecasting (ECMWF) reanalysis product. Ten years of downscaled data are available via the prototype, but the historical downscaled data are being recomputed and extended based on observation/model output comparisons.

Back end programs to run the system are fully functional and statistical collection and graphing of the output is automated. We are currently communicating with a variety of users to determine the best output formats/statistics to use. Examples of output statistics include: percent time impacted, percent time impacted above a threshold concentration, maximum concentration at location during the entire selected time period, average concentration.

Several point source types are available, including wildfire, prescribed burn, and constant emissions source. Additional source profiles need to be collected but are easily added to the system in order to make it more versatile and customized.

Examination of output results show significant inter-annual variability in dispersion patterns from the same source. Statistically significant trends have not been identified at this point, partially due to the limited time period (10 years) currently available. We are currently investigating whether dispersion patterns can be statistically associated with know inter-annual climate variability patterns such as the El Nino Southern Oscillation.

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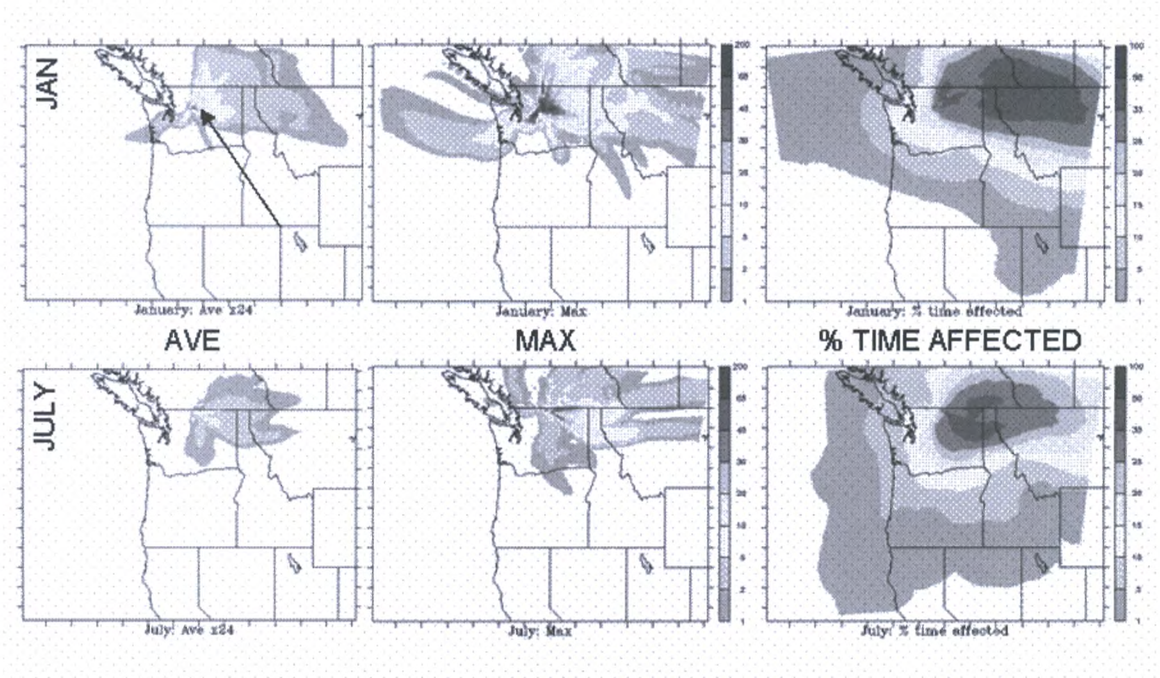
Figure 1. Sample of statistically aggregated output for PM2.5 impacts from a wildland fire. In this example a fire (location indicated by arrow) was run every day during multiple years of Januarys and Julys. Differences between the dispersion patterns in January and July are seen. Average, maximum, and % time affected (concentration > 0) are shown.



Modeling Air Quality Effects of Prescribed Burn in Georgia with CMAQ-Daysmoke

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Abstract

Prescribed burn of forest and other ecosystems is extensively used in the Southeast as a management tool for reducing accumulation of understory debris and maintaining ecosystem health(Wade et al. 2000) . Emissions from prescribed burn are an important source of air pollutants in the Southeast, a region with some of the highest levels of PM and ozone in the nation (Zheng et al. 2002). To evaluate the air quality effects of prescribed forest burn in this region, a modeling tool has been constructed at the USDA Forest Service Southern High-Resolution Modeling Consortium 4S (Achtemeier et al. 2003), which simulates smoke transport and dispersion and the related chemical and physical processes using the Community Multiscale Air Quality (CMAQ) model (Byun and Ching 1999). A unique feature with this modeling tool is the coupling of Daysmoke, a dynamical model to simulate movement and deposition of smoke particles, to provide smoke plume rise (Achtemeier 1998). In Daysmoke, the plume is assumed to be a succession of rising turrets. Detrainment occurs when stochastic plume turbulence places particles beyond plume boundaries. Eddies are two-dimensional and oriented normal to the axis of the mean layer flow. Particles passing a "wall" seven miles downwind from a burning are counted for each hour during the burning period. CMAQ-Daysmoke will assist fire and air quality managers and policy makers in meeting air quality regulations and defining implementation plans. This study illustrates the capacity and sensitivity with CMAQ-Daysmoke through modeling prescribed burn in Georgia on March 6, 2002.

Two burns occurred in Central Georgia with the areas of 856 acres and 420 acres, respectively. Emissions were estimated with the emission models. The simulation domain has 100X100 grid points with a resolution of 12km and 21 layers. The CMAQ vertical component of the grid had 21 layers. The inputs in the Sparse Matrix Operator Kernel Emissions Modeling System (SMOKE) (Houyoux et al. 2002), a model to process emission data and provide initial and boundary chemical conditions for CMAQ modeling, include $PM_{2.5}$, PM_{10}, SO_2, CO, NOx, NH_3, and VOC. The first five compounds were obtained from burning emission data. The two other compounds were specified based on the values in the 1999 EPA National Emissions Inventory. The Carbon Bond-IV (CB-IV) chemical mechanism was used to simulate gas-phase chemistry in CMAQ. Meteorology was simulated with MM5 using the Kain-Fritsch (1993) convective parameterization, the Medium Range Forecast boundary layer scheme(Hong and Pan 1996), the simple ice microphysics scheme and a 5-layer soil model for the land surface scheme. The MM5 outputs were processed through the Meteorology-Chemistry Interface Processor (MCIP) v2.2 for use of SMOKE and CMAQ.

The simulated plume rise is about 0.2 km at 1000 and 1100 LST (Fig.1). Then it rapidly increases to about 1.4 km and remains near this height throughout the afternoon. Most smoke particles are distributed in the upper portion of the smoke plume. The largest $PM_{2.5}$ concentration of over 10 micrograms m^{-3} is found at the grid where the burns are located. The smoke particles are transported northeastward by the prevailing winds (Fig.2). It is found that the specification of smoke plume rise and vertical profile is one of the major uncertainties in modeling the air quality effects of prescribed burn with CMAQ-Daysmoke. Sensitivity experiments are conducted to understand the uncertainties.

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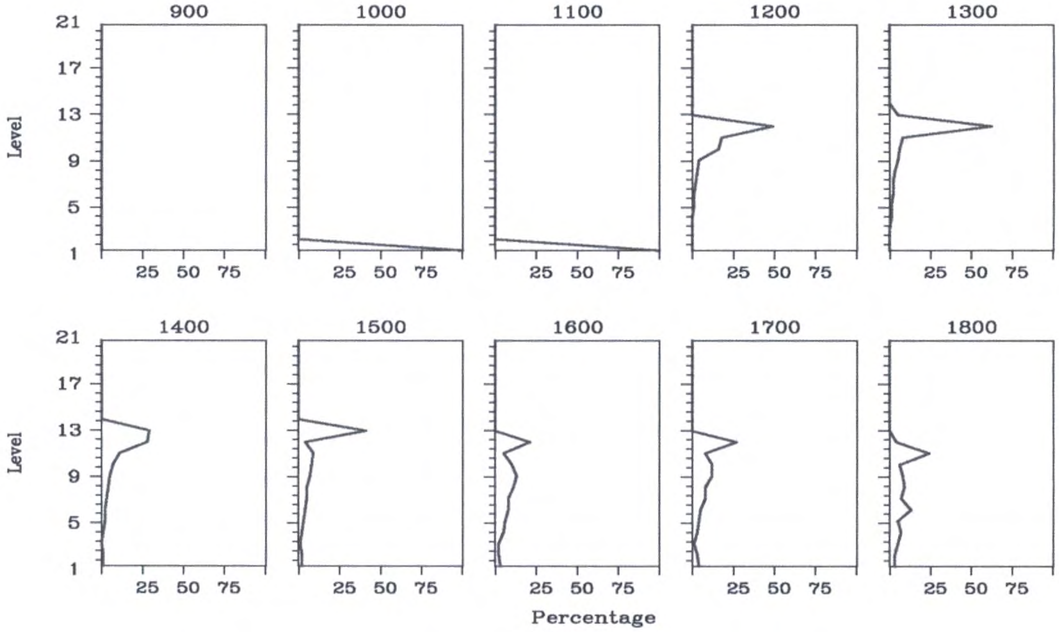

Figure. 1 Vertical distributions of smoke particles estimated using Daysmoke

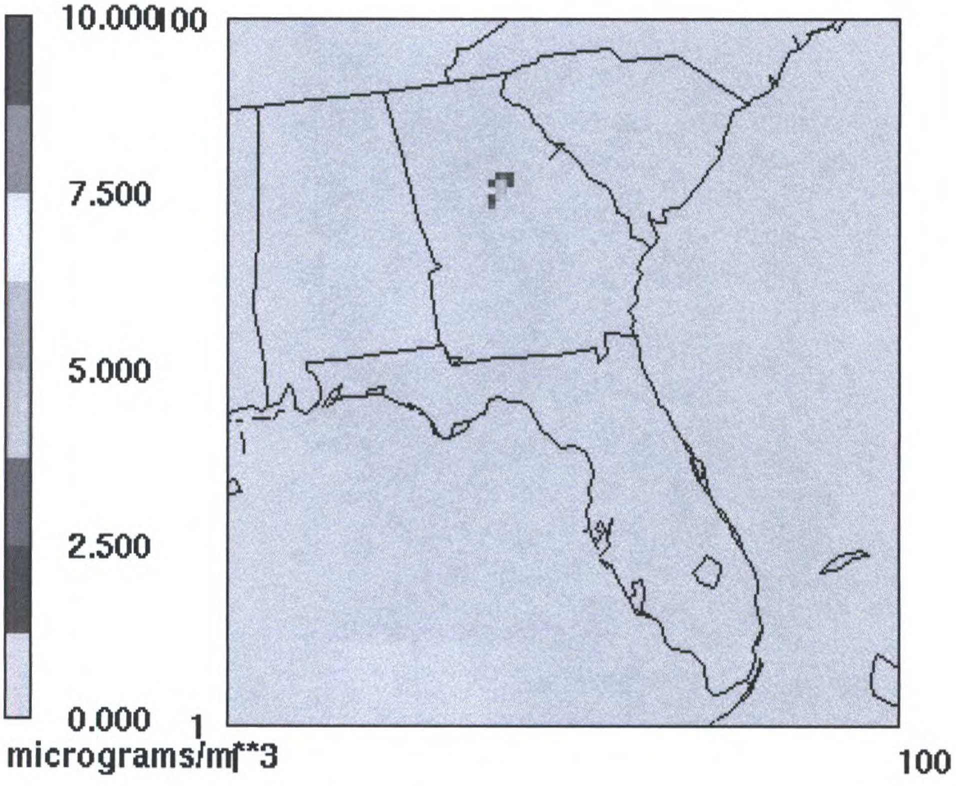

Figure. 2 Ground $PM_{2.5}$ concentration at 1400 LST

Remotely Sensed Measurements of Air Quality Emissions from Agricultural Biomass Burning in the Contiguous United States

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Abstract

On an annual basis, approximately 12% of all fires detected by the Moderate Resolution Imaging Spectroradiometer (MODIS) in the contiguous United States occur in croplands. These fires have received little attention in the scientific literature, yet they impact local and regional air quality. This project will analyze the seasonal and interannual variability of air quality emissions from crop residue burning in the contiguous United States for the years 2004 through 2007. Satellite measures of crop types and burned area will be combined with crop-type specific emission factors for atmospheric species, included in the 1990 Clean Air Act, to quantify air quality emissions. These estimates will support the improvement of the EPA's National Emissions Inventory (NEI) by estimating spatially and temporally explicit emissions. Reported national emissions will be compared with the new estimates to identify areas of discrepancy and evaluate uncertainty in the findings. Additionally, MODIS AOT (aerosol optical thickness) and Aerosol Robotic Network (AERONET) data will be used to characterize the contribution of cropland burning to aerosol optical thickness and air quality and assess the accuracy of the land-based air quality emissions estimates. Preliminary analyses for a case study of agricultural burning along the Mississippi Delta area of Arkansas and surrounding areas in Tennessee and Mississippi will be presented.

Odor

Identification and Quantification of Odorants from Livestock Production by Sampling on Adsorption Tubes and Analysis by Thermal Desorption and Gas Chromatography with Mass Spectrometry

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Abstract

Odour nuisance is a major barrier to the further development of livestock production in Denmark and other livestock-dense areas, and there is an urgent need to develop odour abatement technologies in this field. A first and necessary step is to identify the major odour contributors from livestock production. Three techniques have been chosen for further development: (i) sampling on adsorption tubes with subsequent thermal desorption and analysis by gas chromatography and mass spectrometry (TD-GC/MS), (ii) membrane inlet mass spectrometry (MIMS), and (iii) sampling on adsorption tubes with subsequent thermal desorption and separation by gas chromatography whereby the sample stream is split into a mass spectrometer and a sniffing device with two ports (TD-GC/MS/O). The latter two techniques are presented in other papers; this paper will focus on TD-GC/MS. The objective was to develop a robust and cost-effective technique whereby the sampling can be done by a technician after a very brief period of training and the tubes are sent by mail to the laboratories for further analysis. The result is a method of active sampling on stainless steel adsorption tubes packed with Tenax TA, Carbograph 1TD and Carbograph 5TD or Unicarb. A calibration standard solution containing 40 compounds selected on the basis of their odour contribution values, i.e. typical concentration values divided by their odour threshold concentrations, has been set up and tested. The compounds represent the following chemical groups: sulfides, terpenes, aldehydes, ketones, alcohols, phenols, indoles and volatile fatty acids. The maximum calibration amounts were 100 ng for all compounds except acetic, propanoic, butanoic and pentanoic acids, where 1000 ng were spiked on the adsorption tubes. Twenty to 100 ng were loaded on the analytical column due to a cold trap outlet split of 1:4. The sample separation was performed using a polar polyethylene glycol capillary column. Dimethyl sulphide, methanethiol and trimethylamine were purchased as certified ultra pure gases in nitrogen and added to the adsorption tubes using a gastight syringe. Data for break-through volumes, storage recoveries, desorption efficiencies, method detection limits and GC/MS parameters will be presented. The developed method was used to establish livestock production emission data for the odorants and to evaluate odour abatement technology, e.g. biofilters, wet scrubbers and changes in the feedstuff composition.

Characterization of Dairy Manure Odor Using Headspace Solid Phase Microextraction and Multidimensional Gas Chromatography - Mass Spectrometry - Olfactometry Analysis

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Abstract

Livestock operations are associated with emissions of odor, gases, and particulate matter. The majority of previous livestock odor studies focused on swine operations. Relatively few relate to dairy cattle. Dairy industry in Iowa is sizable (~250,000 head) and modernizing. In Israel, dairy is one of the main livestock production sectors. Thus, there is a need to characterize emissions of odor and odorous gases associated with dairy cattle to enable researchers, industry, and policy makers to better address such aerial emissions. Finding compounds which constitute the primary odor impact is among the most demanding of analytical challenges because critical odor components frequently present at very low levels in a complex matrix of numerous insignificant volatiles. In this study dairy manure odor was characterized using a novel multidimensional gas chromatography - mass spectrometry - olfactometry (MDGC-MS-O) system allowing for simultaneous chemical and sensory analyses of dairy odors. Manure samples were collected from the ISU Dairy Farm in Ankeny, Iowa. Headspace solid phase microextraction (HS-SPME) was used to collect volatiles from 3 mL manure enclosed in 20 mL vials held at 30 °C. A total of 25 extractions ranging from 15 sec to 11 h using DVB/Carboxen/PDMS fibers were completed. These were followed by chemical-olfactory analyses on the MDGC-MS-O system. Multidimensional capability of the analytical system enabled the isolation and identification of key characteristic odorants. To date, more than 50 distinct odors/aromas and over 150 compounds were found emitted from dairy manure. Of these, about 20 odor-compounds matches were already resolved and more are underway. Several key characteristic odorants were matched and identified. These include S-containing compounds (i.e. dimethyl sulfide / onion; dimethyldisulfide / sweet; dimethyltrisulfide / garlic), volatile fatty acids (i.e. butanoic acid / cheesy, body odor; pentanoic acid / body odor) and phenolic compounds (i.e. p-cresol / medicinal, barnyard; indole / phenolic, body odor; skatole / phenolic, body odor). Both short and long HS-SPME exposure times resulted in clear separations of MS and aroma peaks that were also important odorants. At very short extraction times sulfuric and phenolic compounds were most dominant. Odor intensity and the number of compounds identified were generally proportional to the SPME extraction time. Compound competition and displacement was delineated for several VOCs particularly during longer extraction times. Different relationships between compound concentrations (MS peak area) and intensity of their matched odor (aroma peak area) were also observed. These relationships were more strongly dependent at short extractions.

Quantification of Odor and Odorants at Swine Facilities and Assessment of Their Impact Downwind

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Abstract

Confinement swine production has been developed to increase productivity and to make efficient use of land and facilities. However, complaints of malodors are reported with increasing frequency in some communities near confined swine operations. The purpose of this paper is threefold: 1) to describe methods for quantifying odor and odorants emitted at swine operations, 2) to show how the odor is typically dispersed downwind, and 3) to elucidate the potential impact on human health from exposure to odor (and odorant) levels to which a neighbor is typically exposed. Methods used to quantify odor and odorants include: a) human assessments of the odors and irritation associated with gaseous emissions and particulates, and b) instrumental measurements of the concentrations of total volatile organic compounds (called VOCs), hydrogen sulfide, ammonia, particulates, and endotoxin present in the air during the odor assessments. Human evaluations of odor and irritation in the field are obtained with portable threshold devices (e.g. Scentometer, Nasal Ranger®, Duke University lateralization device), comparison with butanol standards, and ratings of overall odor intensity, irritation intensity, pleasantness, and odor character. Air samples are also obtained in the field in Tedlar® bags which are taken to the laboratory for olfactometry to determine how many times the odorous air needs to be diluted to reach threshold. The olfactometer utilized has a variety of testing modes including Triangular Forced Choice and meets the requirements of the CEN odor testing standard, EN13725:2003 and ASTM International E679-91. VOCs are measured in two ways. Real-time monitoring of VOCs at ppb levels is performed with a photo-ionization detector (PID) that can detect VOC concentrations down to a few ppb. Air samples are also obtained in canisters and analyzed in the laboratory by GC/MS and GC/FID. Hydrogen sulfide is measured with a gold film sensor selective for hydrogen sulfide. Ammonia is measured with a chemiluminescence NH_3 analyzer and Draeger tubes. Total suspended particulate concentrations are measured in real time by a monitor that utilizes aerodynamic particle sizing and an in-line filter cassette for gravimetric sampling (HAZ-DUST EPAM-5000). Endotoxin is collected on fiberglass filters and quantified using a Limulus Amebocyte Lysate (LAL) assay. Human measurements are correlated with instrumental measurements to determine the best predictors of odor. Dispersion modeling is used to predict the intensity of odor and concentration of odorants downwind under a variety of atmospheric conditions. Levels downwind predicted by dispersion modeling are compared with results from exposure studies to determine potential health effects.

This paper will present research findings that compare odor dispersion from swine facilities that used a variety of alternative and conventional waste technologies. Nineteen different sites were included in the study; some sites included more than one technology to be evaluated. The trajectory and spatial distribution of odor and odorants downwind of each of the facilities (the alternative technologies and two controls) under two meteorological conditions (daytime and nighttime) were predicted using a Eulerian-Lagrangian model. The odor modeling was based on a mathematical model to predict long distance dispersion (Hsieh et al. 1997; Katul and Albertson, 1998; Nathan et al., 2002; Hsieh et al., 2003) but was modified to be consistent with experimental odor dispersion data at swine operations in North Carolina (Schiffman et al., 2003a; Schiffman et al., 2003b; Schiffman et al., 2005). Modeling was performed using all significant odor sources at a facility. This model was strengthened during the course of the study with an increased number of testing sites and observations. For the farms with animals, the computations were performed with and without the swine houses to determine the odor contribution from the animals themselves along with the technology components. The potential health consequences of the levels of odors dispersed downwind will be addressed as well.

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1000 Olfactometry Analyses and 100 TD-GC/MS Analyses to Evaluate Methods for Reducing Odour from Finishing Units in Denmark

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Abstract

Odour from pig production is one of the biggest barriers to expanding pig production units in Denmark. There is a great need to develop methods to reduce odour emission. However, it is very important that the solutions are economically feasible. During the last four years, the National Committee for Pig Production has carried out approximately 1000 olfactometry analyses of air samples from commercial pig production units. The measurements have primarily been carried out in finishing units because approximately 70% of odour originates from this part of an integrated pig production unit.

The aim was to evaluate different methods for reducing the odour emission. Case-control studies were performed to test different methods, and an intensive campaign measurement programme was conducted to investigate whether an idea for odour reduction has a potential for development.

In the case-control studies, the farms were visited every second week over a period of six months. Each time, the following samples and registrations were made: 1) air sample was collected in 30-litre tedlar bags during a 40-minute period, and analysed in accordance with European CEN standard for olfactometry the following day, 2) ventilation rate was determined using calibration measuring fans from Fancom and 3) ammonia and carbon dioxide concentrations were measured using detection tubes from Kitagawa and electronic equipment from the Veng system. During the last year of the project, the measurement protocol was enlarged to include sampling on adsorption tubes and analysis by gas chromatography and mass spectrometry (TD-GS/MS).

The overall conclusions of the tests were that 1) The odour emission is 3-5 times higher during the summer than during the winter, 2) There is a linear correlation between air exchange and odour emission, 3) The odour emission from a finishing unit with slurry system is the same before and after delivery of pigs as long as the ventilation rate is maintained, 4) Management factors are essential for controlling the odour emission from finishing units. 5) Biological purification of exhausted air is the only odour-cleaning technique that can be recommended, 6) Scrubbers with one filter using sulphuric acid can only be used for ammonia reduction and not for odour reduction, 7) comparison of odour strengths determined by olfactometry and TD-GS/MS indicated that phenols, indoles and volatile fatty acids do not play a major role for the odour emission. This part will be discussed in the presentation, however not in the proceedings.

Introduction

Denmark is a small country in Europe that produces 25 million pigs annually, corresponding to the number of pigs raised in Iowa. However, in terms of land area, the country is only 1/3 of the size of Iowa and has twice the human population.

As in every other industrial country with a high pig density compared with the human population density, odour has become an increasing problem. If production levels are to be maintained or even increased, it is essential to develop methods for reducing odour.

Meat-exporting countries such as Denmark cannot add the cost of reducing odour to the retail price. Importing countries will not pay for odour reduction in Denmark. Therefore, odour reduction in industrial countries with high pig densities compared with human population densities has to be financed by achieving a higher level of productivity within pig production, enhancing the quality of the meat and, last but not least, improving the country's veterinary health status and food safety standards. If these criteria cannot be met, the pig production sector will move to countries with lower human population densities and fewer environmental regulations.

In the light of this scenario, the National Committee for Pig Production, Danish Bacon and Meat Council, has conducted and financed a number of campaign measurements and specific tests aimed at following new technology and shortening the path from idea to reliable and cost-effective odour reduction method.

Today, ammonia emissions can be reduced by 90%. When odour from pig housing facilities can be reduced by more than 90-95% and demands for operating efficiency and cost-effectiveness have been met, there will be a strong potential for growth in pig production.

Aim

The aim of the paper is to present the results from a number of projects that were conducted in order to evaluate different methods for reducing odour from finishing units in Denmark. The proceeding will involve analyses of:

- Feed experiments
- Ventilation rate
- Chemical air purification
- Biological air purification
- Odour source

Besides the tests of odour reduction technologies, some supplementary experiments were conducted in order to answer the following questions:

- Is it possible to mail odour samples in Tedlar bags from a post office near the farm to the olfactometry laboratory during the cold winter period, when there is a risk of condensation forming inside the bags?
- How many odour measurements need to be taken in a case-control study in order to demonstrate a difference of 50% between the emissions from two sections?

Materials and Methods

The odour tests of different techniques were performed in commercial pig herds around Denmark, and the feed experiments and cooling experiment were performed at a test station owned by Danish Bacon and Meat Council.

All measurements were taken in finishing units, since 70% of the odour from an integrated production facility comes from the finishing unit. This can be seen both in the use of current standard data for odour emissions from pig units, which are based on measurements taken in German housing units in the 1980s, and in the future standard data for odour emissions from pig units, which are based on Danish measurements taken in 2005 (reference 1).

Two different test protocols were used in the testing of the different technologies:

- One of the protocols is referred to as campaign measurements, which are designed to show whether an idea for odour reduction has a potential for development. The evaluation is based on an intensive measurement programme spread over a period of one and a half months.
- The other protocol is referred to as a case-control study, which is designed to demonstrate to the environmental authorities and the pig producers the capability of a technology. This study is spread over a period of at least six months so that different seasonal variations and operating efficiencies can be included. During this period, odour concentrations were measured every two weeks.

The primary test parameter was the odour emission. The odour concentration was measured by collecting exhausted air in a 30-litre Tedlar bag during a 40-minute period.

The following day, the air bags were analysed at the Danish Meat Research Institute to determine the odour concentration using the olfactometric method in accordance with the European CEN-standard (reference 2).

In connection with the odour samplings, the following data were registered in all the case-control studies and some of the campaign measurements:

- Ventilation rate (using Fancom measure wings)
- Carbon dioxide concentration in the chimney (using Kitagawa tubes and pump)
- Ammonia concentration in the chimney (using Kitagawa tubes and pump)
- Outdoor temperature and the temperatures in the chimneys
- Number of pigs at pen level and visual assessment of the weight of the pigs
- Chemical substances sampled together with some of the odour samplings (TD-GC/MS)

In the case-control studies, the temperatures, ammonia concentrations, carbon dioxide concentrations, and in some cases, ventilation rate were also measured online once an hour using the Danish Veng system.

This equipment consisted of pumps, that pumped approximately two litres of air per minute from the air inlet and chimneys through Teflon tubes to instruments that analysed the ammonia and carbon dioxide content of the air. To measure the ammonia concentration, a Polytron 1 from Dräger with a measuring range of 0-100 ppm was used, and to measure the carbon dioxide concentration, a Vaisala with measuring range of 0-5000 ppm was used.

A manifold placed immediately before the ammonia and carbon dioxide instruments ensured that the air from each pump was sent separately to the two instruments. The air from each pump was analysed for a period of ten minutes, and the last recorded value was stored.

During every second measuring period, outdoor air was pumped through the ammonia and carbon dioxide instruments. All the air that was analysed was preheated to 34 °C, before being pumped into the measuring instruments.

The reason for choosing to send the outdoor air through the instruments every second time and to preheat the air from the measuring points in the pig unit was to make the ammonia sensor stable.

There had previously been problems maintaining the calibration, especially when the relative humidity in the unit was high. The preheating was carried out by placing the manifold in a steel box that could be heated electrically.

Statistics for Case-Control Studies

Emissions of ammonia and odour were determined by multiplying the odour concentrations by the ventilation rate.

For each batch, the average and standard deviation were determined for the temperature in the chimney, ventilation rate, carbon dioxide concentration, and the concentration and emission of ammonia.

For the latest case-control studies, the log-transformed odour emission was analysed statistically using a variance analysis in the MIXED procedure in SAS. The group and batch were included as a systematic effect.

Supplementary Experiment 1 – Condensation

Since the odour samples were taken in Tedlar bags at different pig units around Denmark, it would have been time-consuming for the technicians to deliver the samples to the olfactometry laboratory. Instead, the samples were sent to the institute by express mail. However, according to the CEN-norm condensation is not allowed in the bags, and there was a risk of condensation at low outdoor temperatures. A supplementary experiment was therefore performed to investigate what effect the condensation would have on the actual analysis.

The simulation was carried out as follows. Three double samples were taken between 12 pm and 1 pm, 1pm and 2 pm, and 2 pm and 3 pm, respectively. At 4 pm, one of the double samples was placed in a freezer at a temperature of -3°C, while the other sample was kept at 22°C. At 9 am the following morning the bags were taken out of the freezer and placed next to the other bags. The odour analysis was started at 12 pm. The experiment was repeated the following days.

Supplementary Experiment 2 – Panel Variation

Generally speaking, there has been a lot of scepticism about panel variation when analysing odour from pig units. For this reason, a comparative study of the two panels was conducted.

The air samples were analysed twice, first by a panel in the morning and then by a panel in the afternoon. The analysed samples were taken from the chimney in two identical housing sections for finishing pigs. A total of 36 measurements were analysed twice by different panels.

Supplementary Experiment 3 – Statistically Significant Difference Between Two Systems

Before starting an experiment, it is necessary to know how many measurements need to be taken to prove a statistically significant difference between systems.

Over a period of one year, odour measurements were taken at regular intervals in two identical sections for finishing pigs. A total of 4 batches were included in the experiment. For each batch measurements were taken on 5 to 7 occasions and each time odour measurements were taken between 12 pm and 1 pm, 1pm and 2 pm, and 2 pm and 3 pm. Besides odour, the registration parameters mentioned previously were also recorded.

In the statistical calculations, the percentage difference between the odour emission in the two sections was considered. A variance analysis was performed in order to determine the number of measurements needed to record a difference of 50, 30 and 20% between the sections, depending on the number of measurements taken each day.

Results and Discussion of Supplementary Experiments

Results and discussion for the supplementary experiments will be given before the odour reduction technologies, because the supplementary experiments form the basis of the overall measurement strategy.

Supplementary Experiment 1 – Condensation

In supplementary experiment 1, in which condensation in the Tedlar bags was simulated, visible condensation on 1/5-1/2 of the inner surface of the bag was recorded, when they were taken out of the freezer at 9 am. At the start of the odour analysis at 12 pm, the temperature in all of the bags was 22.5 °C, so no condensation was present at the time of analysis. The results of the odour analysis are illustrated in Figure 1. The odour analysis showed, that at the specified temperature and humidity levels, the presence of condensation had no effect on the result of the odour analysis.

Provided there is no condensation when the samples are taken in the pig unit and at the time of analysis, then it makes no difference if there is condensation in the period between sampling and analysis. It was therefore concluded that odour samples can be sent by express mail to the olfactometry laboratory.

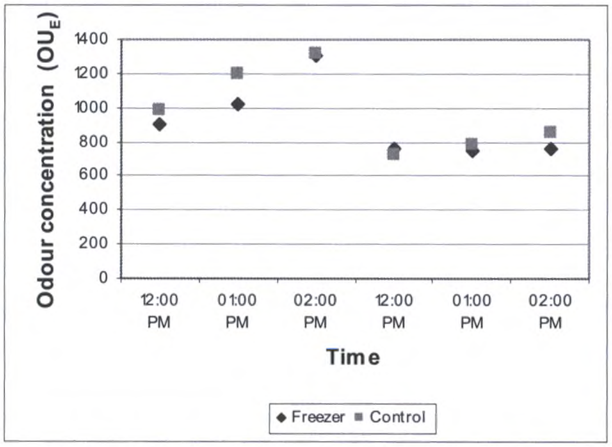


Figure 1. The odour concentration in Odour Units (OU$_E$) for the double air samples, one of which was kept in a freezer at – 3°C and the other at 22 °C. When the samples were analysed, the temperature was 22.5°C. The samples were taken over a period of two days between 12 pm and 1 pm, 1pm and 2 pm, and 2 pm and 3 pm, respectively. The temperature in the pig unit was 18°C and the relative humidity was 68%.

Supplementary Experiment 2 – Panel Variation

The results of double olfactometry analysis for 6 days' odour measurements in two sections for finishing pigs are shown in Table 1.

The log-transformed odour concentration was analysed statistically using a variance analysis in the MIXED procedure in SAS. The time of day and section were included as a systematic effect, and the date and panel within the day were included as a random effect.

The estimate of the covariance parameter shows that 79% of the variance of the odour concentration is caused by the date, 10% is caused by the section, and that the panels do not contribute to the variance.

After this calculation, the percentage difference between the odour concentration recorded by the morning panel and the afternoon panel was calculated for each bag with odour.

Then the calculated differences were then analysed statistically using a variance analysis in the MIXED procedure in SAS. The time of day and section were included as a systematic effect, and date was included as a random effect. The result showed that 95% confidence interval for the percentage difference between the panels was -10 – 9%.

It can be concluded that, compared to the variance of date and compared to the difference of the sections, the variance of the panels can be neglected. It can also be concluded that 95% of the differences between the panels were within the interval of -10 – 9%.

Table 1. Odour concentration analysed twice by a morning panel and an afternoon panel, respectively.

	Time	12 pm – 1 pm		2 pm – 3 pm		4 pm - 5 pm	
	Section	1	2	1	2	1	2
3 Sept	Morning	577	869	633	654	745	739
	Afternoon	633	630	702	770	604	680
18 Sept	Morning	1272	950	1275	948	1142	782
	Afternoon	1219	776	1329	1078	1521	707
2 Oct	Morning	716	618	618	750	908	471
	Afternoon	811	594	871	746	748	668
16 Oct	Morning	1512	2258	2602	1629	1998	2041
	Afternoon	1851	1918	2345	1578	1853	1318
30 Oct	Morning	1105	1029	1145	1035	993	1392
	Afternoon	1025	1145	993	893	1002	1502
11 Nov	Morning	623	817	724	701	658	754
	Afternoon	722	744	812	865	744	981

Supplementary Experiment 3 – Statistically Significant Difference Between Two Systems

Odour emissions from two identical sections for finishing pigs over a period of one year are shown in Figure 2. Figure 3 shows the percentage difference in odour emission between the two sections. As can be seen in the graph in Figure 3, the percentage differences vary around 0, and in table 2 the average and standard deviation are shown for each batch.

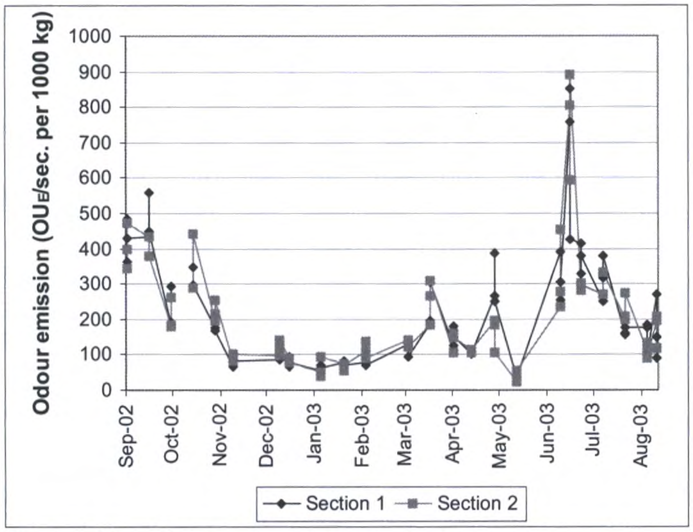


Figure 2. Odour emission in OU$_E$/sec. per. 1000 kg animal. On one measurement day (18 June), the odour emissions were inexplicably high. Presumably, the measurements taken on this day are incorrect.

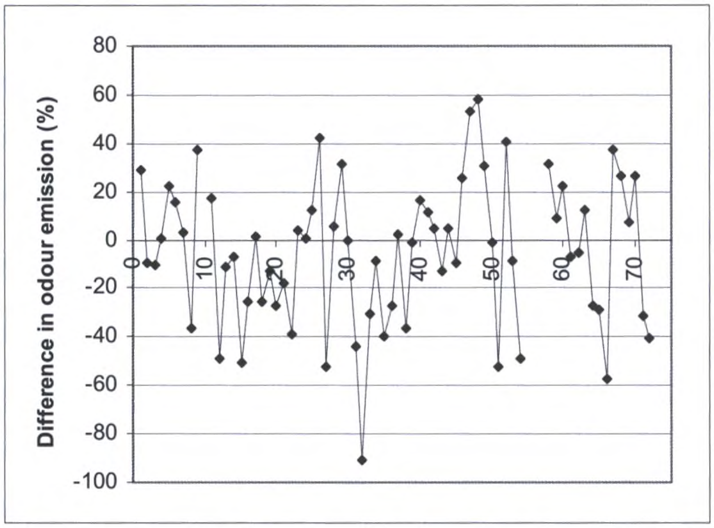


Figure 3. Differences in odour emissions between the odour samples taken in the two sections at the same time. A total of 144 odour measurements were taken, i.e. 72 pair-wise registrations. Data from 18 June are not included in the figure, because of the inexplicably high values on this day.

Table 2. Odour emissions from two identical sections for finishing pigs.

Batch	Average of odour emissions		Average of percentage difference between the odour emissions registered at the same time in section 1 and 2	Standard deviation of the percentage difference between the odour emissions taken at the same time in section 1 and 2
	(OU_E/sec. pr. 1000 kg)		(%)	(%)
	Section 1	Section 2		
1 Sep-Nov	284	280	1.4	26
2 Dec-Feb	78	90	-15	34
3 Mar-May	157	140	9	30
4 June-Aug	310	314	-1.2	38
4 Without the divergent measurements the 18 June	248	238	-2.4	31

Despite the large differences in odour emissions from batch to batch shown columns 2 and 3 in Table 2, it was interesting to observe that the standard deviations of the percentage differences between the odour emissions from the two sections were at the same level for each batch throughout the year.

If the three percentage differences in odour emissions from the same day are seen as repetitions, and the entire data set is taken into account, the variance between days is 234 and the variance within the day is 675. This means that 74% of the variance of the percentage differences in odour emissions from the two sections is due to the variation within the day.

Measurements taken over a period of one year can be used to predict the number of measurements needed to determine whether a given treatment is capable of reducing odour emissions by 50, 30 and 20%, respectively. If the variation between days is set to 27 and the standard deviation is set to 35, then, for example, 10 days with one measurement in each section, or 6 days with triple measurements in each section are needed to test a 50% reduction (see Table 3).

Table 3. Number of measurements needed to test a difference in odour emission from two identical sections with different treatments

Reduction (%)	1 sample in each section per day	2 samples in each section per day	3 samples in each section per day
50	10	8	6
30	24	16	13
20	50	33	28

Results and Discussion of Test Concerning Odour Reduction Technologies

Feed Experiments

Three feed experiments were carried out at the test station owned by Danish Bacon and Meat Council. Before describing the results in detail, it should be mentioned that none of the feed experiments had an effect on the odour emission. However, as expected the experiments resulted in reduced ammonia emissions.

Crude Protein

The odour and ammonia concentrations in two sections with finishing pigs weighing between 33 and 113 kg were compared. In one of the sections, the pigs were fed a diet containing a reduced level of crude protein. The feed was delivered to the farm in two batches. The analyses showed that the first delivery for sections 1 and 2 contained 16.1 and 14.2% crude protein, respectively, and the second delivery contained 15.1 and 14.0%, respectively.

The ammonia concentration and the secondary registration parameters using the Veng system were taken every half hour. Three odour samples were collected in the chimney in each of the two sections on 6 measurement days spread over the whole production cycle.

The ammonia emission was reduced by 33% in the section with the reduced level of crude protein. With the given number of measurements, it should be possible to prove whether treatment with reduced crude protein could reduce the odour emission by 50%, but in this experiment it was not possible.

Table 4. Average of ammonia and odour emission together with supplementary records in the experiments with different levels of crude protein

Section	Ambient temperature	Outlet temperature	Ventilation rate	NH_3	CO_2	Ammonia emission		Odour Emission
	Celsius	Celsius	m^3/hour per pig	ppm	ppm	g NH_3-N/hour	kg NH_3-N	OU_E/sec. per 1000 kg
Control	-0,1	17.3	27	19.8	2316	0.304	0.533	78
Reduced crude protein		16.3	29	12.5***	2232	0.209***	0.366***	90

*, **, ***: Statistically significant difference, *: $P<0.05$; **: $P<0.01$; ***: $P<0.001$

Benzoic Acid

The feed containing 1% benzoic acid was tested on pigs weighing between 30 and 100 kg, while feed containing 3% benzoic acid was tested on pigs weighing between 65 and100 kg.

Batch 1: Control feed versus control feed containing 1% benzoic acid.

Batch 2: The same as batch 1, though the treatments in the sections were interchanged.

Batch 3: Control feed versus control feed containing 3% benzoic acid.

Batch 4: The same as batch 3, though the treatments in the sections were interchanged.

The ammonia concentration and the secondary registration parameters using the Veng system were recorded every half hour.

For both batches 1 and 2, three odour measurements were taken in the chimney in each of the two sections on 6 measurement days spread over the whole production cycle. For both batches 3 and 4, three odour measurements were taken in the chimney in each of the two sections on 6 measurement days spread over the two production cycles. This means that, a total of 108 odour measurements were taken.

The addition of benzoic acid to the feed did not result in a statistically significant differerence in the odour emission.

In batch 1, the ammonia emission was 10% higher from the section with the feed containing 1% benzoic acid compared with the control section, where benzoic acid was not added to the feed ($p<0.05$). The reason that there was an increase rather than a reduction is that, according to the feed analyses, the crude protein content in the feed was 0.9% higher in this group. Furthermore, the results of the analysis showed that the concentration of benzoic acid was not 1%, as expected, but rather 0.83%.

In batch 2, the feed mixtures were identical, except for the addition of 1% benzoic acid to the feed in the treatment group, and the experiment showed that the ammonia emission was 5% lower from the unit where the pigs were given feed containing benzoic acid. However, the reduction was not statistically significant.

Table 5. Average of ammonia and odour emission together with supplementary records in the experiments with different levels of benzoic acid added to the diet

Section	Ambient temp.	Outlet temp.	Ventila-tion rate	NH_3	CO_2	Ammonia emission		Odour Emission
	Celsius	Celsius	m^3/hour per pig	ppm	ppm	g NH_3-N/hour	kg NH_3-N	OU_E/sec. per 1000 kg
Batch 1			0					
Control	5.7	17.9	36	16	2154	0.216	0.430	122
1% benzoic acid		17.5	41	14	2030	0.237* (26-100 kg)	0.471*	114
Batch 2								
Control	16.7	21.1	84	4	820	0.171	0.332	255
1% benzoic acid		21.4	79	4	908	0.163 (27-100 kg)	0.317	255
Batch 3								
Control	7.3	17.6	55	15	1518	0.461		207
3% benzoic acid		16.7	59	6	1259	0.182*** (86-100 kg)		288
Batch 4								
Control	5.3	15.5	56	14	1582	0.424		127
3% benzoic acid		16.3	48	7	1665	0.191*** (80-100 kg)		128
Batch 3+4								
Control	6.2	16.5	56	14	1556	0.440		
3% benzoic acid		16.5	53	7	1485	0.187*** (86-100 kg)		

*, **, ***: Statistically significant difference, *: $P<0.05$; **:$P<0.01$; ***:$P<0.001$

In batches 3 and 4, where 3% benzoic acid was added to the feed given to the treatment group, there was a 58% reduction in the ammonia emission during the last part of the production cycle. The difference was statistically significant ($p<0.001$).

The experiment was not designed to prove a difference in production results. However, it should be mentioned that the lowest production results were found in the group fed a diet containing 3% benzoic acid. In the EU, benzoic acid is approved for use in feed for finishing pigs in doses up to 1%. Dispensation was given for the experiment with 3% benzoic acid.

Coarsely Ground Meal Feed Compared with Finely Ground Pelleted Feed

Coarsely ground meal feed (5 mm hammer mill) was compared with finely ground pelleted feed with regard to odour and ammonia emission. Two batches of pigs weighing between 65 and 100 kg were included in the experiment. The ammonia concentration was measured every half hour. For both batches, three odour measurements were taken in the chimney in each of the two sections on 6 measurement days spread over the two production cycles.

The results of the experiment show that the ammonia emission was higher for coarsely ground meal feed than for the finely ground pelleted feed. On average, the ammonia emission was 20% for the meal feed. The difference was statistically significant (p<0.001). There was no effect on the odour emission.

Table 6. Average of ammonia and odour emission together with supplementary records in the experiments with comparison of coarsely ground meal feed and finely ground pelleted feed (control)

Section	Ambient temperature Celsius	Outlet temperature Celsius	Ventilation rate m^3/hour per pig	NH_3 ppm	CO_2 ppm	Ammonia emission g NH_3-N/hour	Odour Emission OU_E/sec. per 1000 kg
Batch 1							
Control	0.5	17	31	18	2646	0.31	225
coarsely ground meal feed		16	34	21	2404	0.40***	198
Batch 2							
Control	4.8	16	44	13	1826	0.33	178
coarsely ground meal feed		17	40	17	2003	0.39***	146
Batch 1+2							
Control	2.7	16.5	38	16	2236	0.32	200
coarsely ground meal feed		16.5	37	19	2204	0.40***	170

*, **, ***: Statistically significant difference, *: P<0.05; **:P<0.01; ***:P<0.001

Ventilation Rate

The odour emission from the finishing unit with a slurry system is generally 3-5 times higher in the summer than in the winter. This is presumably because of changes in the air exchange in the sections. An experiment was therefore carried out to demonstrate the effect of the air exchange on the odour emission. A constant ventilation rate of 100 m^3/hour per pig (maximum ventilation in finishing unit in Denmark) was compared with a ventilation rate of 50 m^3/hour per pig for two batches of pigs weighing between 64 kg and 104 kg.

A cooling system was installed to cool the inlet air to the section with the reduced ventilation rate so that the desired temperature in the sections could be maintained.

In this experiment, the same measurements as in the feeding experiments were taken.

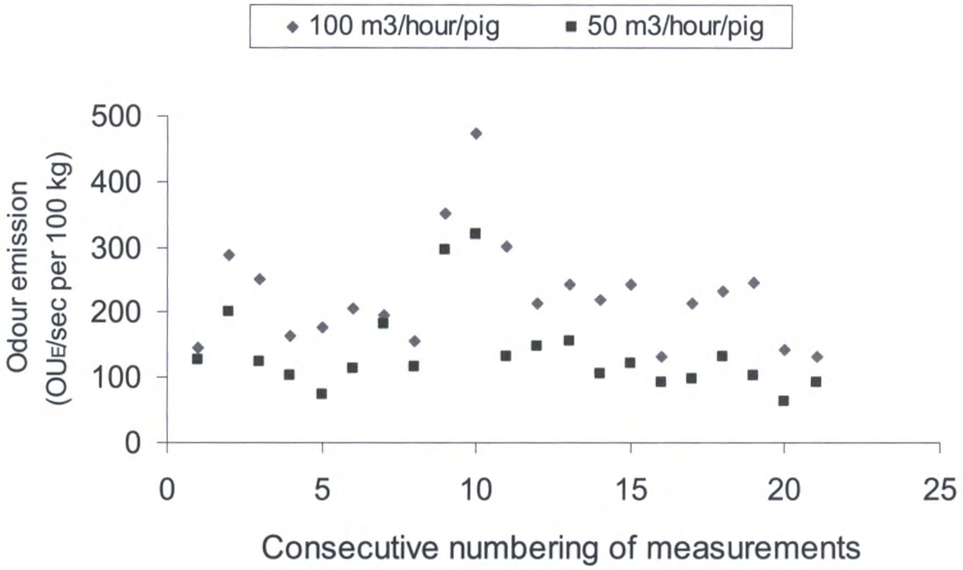


Figure 4. The odour emission from the trial section (50 m^3/hour per pig) with reduced air exchange and the control section with maximum ventilation (100 m^3/hour per pig) for two batches of pigs

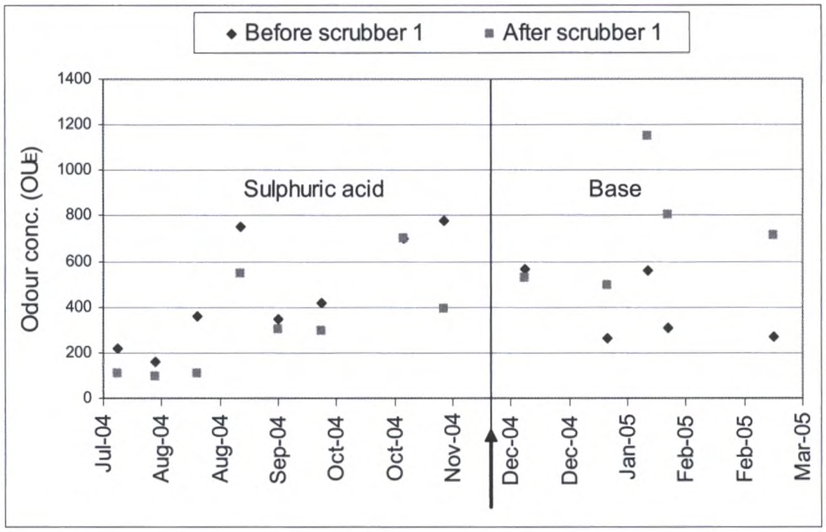
On days with odour measurements, the ventilation rate in the trial section was reduced by an average of 50% in batch 1, and this resulted in an odour reduction of 33% with a 95% confidence interval [21 - 45] compared with the control section. In batch 2 the ventilation rate was reduced by an average of 56% on the odour measuremens days, and this resulted in an odour reduction of 47% with a 95% confidence interval [39 - 54].

The effect of the reduced ventilation rate on the ammonia emission was not as great as on the odour reduction. The ammonia emission from the trial section was reduced by 11% with a 95% confidence interval [8 - 13], while for batch 2 the ammonia emission was reduced by 8% with a 95% confidence interval [4 - 11] compared with the control section.

Chemical Air Purification

Purification of the air with scrubbers using a sulphuric solution has been widely tested in Europe and, for many types, the reduction of ammonia is 90-95%. The companies are also trying to develop the systems, with a view to reducing the odour emission. Also, a number of new chemical liquids for the scrubbers have been introduced. However, campaign measurements before and after the air cleaning system show that the chemical scrubbers have no effect - or a minor effect - on the odour emission (see Figure 5).

A new type of chemical air cleaner based on membrane technology is under development. The idea of the system was last year introduced by four Danes and campaign measurements have shown that the system has considerable potential as a method for reducing odour, as long as the system can be developed at a realistic price. The ammonia and hydrogen sulphide were reduced by more than 95% and the results of the odour measurements are shown in Figure 6.



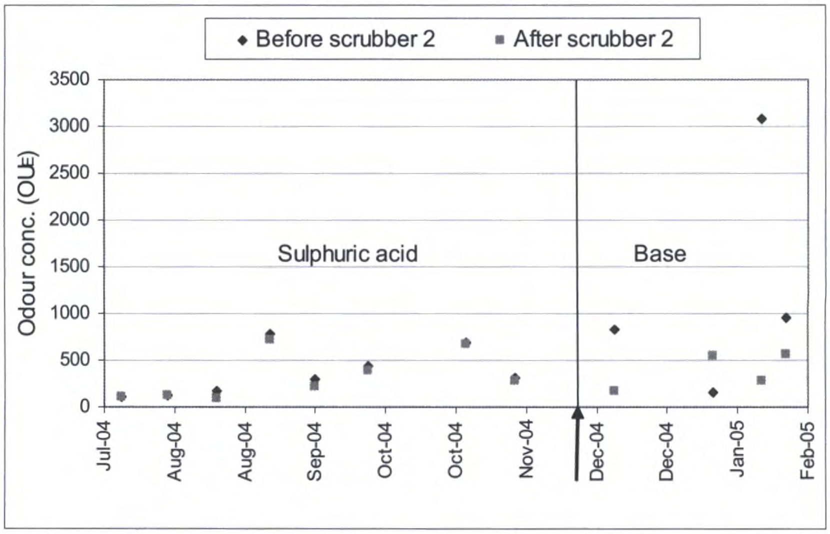


Figure 5. Odour measurements before and after two scrubbers from Scan Airclean A/S. During the first period, a solution containing sulphuric acid was used, and during the last period an alkaline solution was used. The two scrubbers purified the exhausted air from two identical sections at the same farm. However, only one of the scrubbers was able to reduce the odour concentration. In Denmark, the chemical scrubbers using sulphuric acid can only be used for ammonia reduction and not for odour reduction.

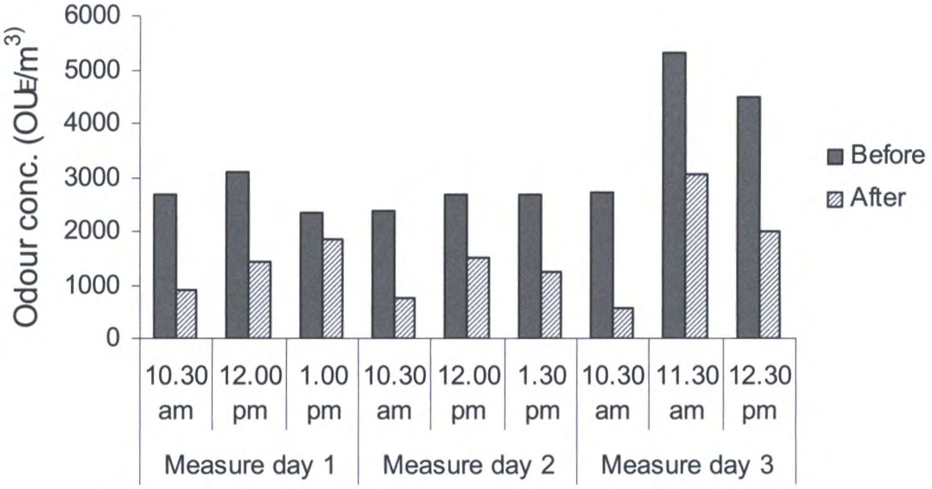


Figure 6. The odour concentration before and after a pilot membrane filter installed after the chimney at a finishing unit. The three measurement days were campaign measurements spread over a 6-weeks period. The positive result demonstrates that the new membrane technology can be used as a odour reduction method in the future.

Biological Air Purification

Two types of biological air purification have been tested. One of the filters is from SKOV A/S and Perstrup Beton Industri A/S and the description and test results are given in the proceeding "A Biotrickling Filter for Removing Ammonia and Odour in Ventilation Air from a Unit with Growing-Finishing Pigs" (reference 3). The other filter is an Oldenburg biofilter, Agrofilter GmbH from Germany.

The Oldenburg biolfilter was installed beside a finishing unit and purified the exhausted air. The biological filter was tested over a period of six months.

The odour reduction is illustrated in Figure 7. The odour reduction was, on average, 49% with a 95% confidence interval [29 – 69]. If the period with problems with the moisture system is excluded the odour reduction was 60% with a 95% confidence interval [37 - 83].

The Oldenburg biofilter required a lot of space. The filter area was 50-60% of the area of the stable. Therefore, the biological filter from SKOV A/S and Perstrup Beton Industri A/S will be more realistic in the future.

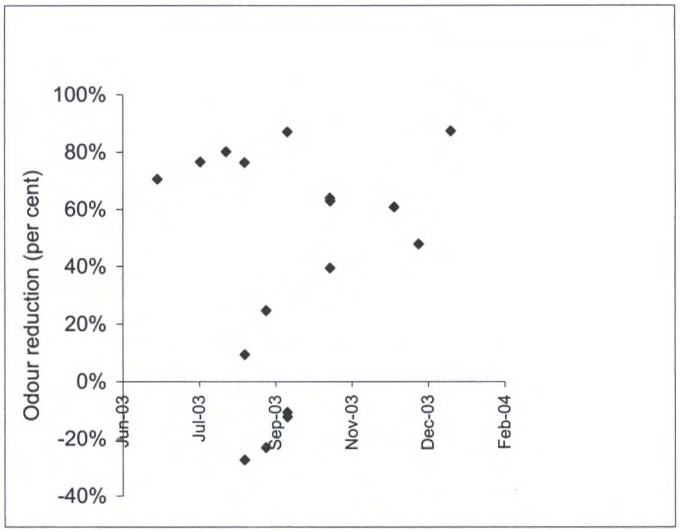


Figure 7. Odour reduction using an Oldenburg Biolfilter, Agrofilter GmbH. The drop in odour reduction was caused by moisture system failure.

Odour Source

To obtain better knowledge of the odour source the odour concentration was measured from two sections before and after delivery of finishing pigs to the slaughterhouse. After the sections had been emptied of pigs, the ventilation rate was maintained at the same level as before delivery.

The measurement results are shown in Figure 8. The odour concentrations before and after delivery of the pigs were approximately the same. This means that most of the odour originates from the slurry pit and manure deposited in the pen.

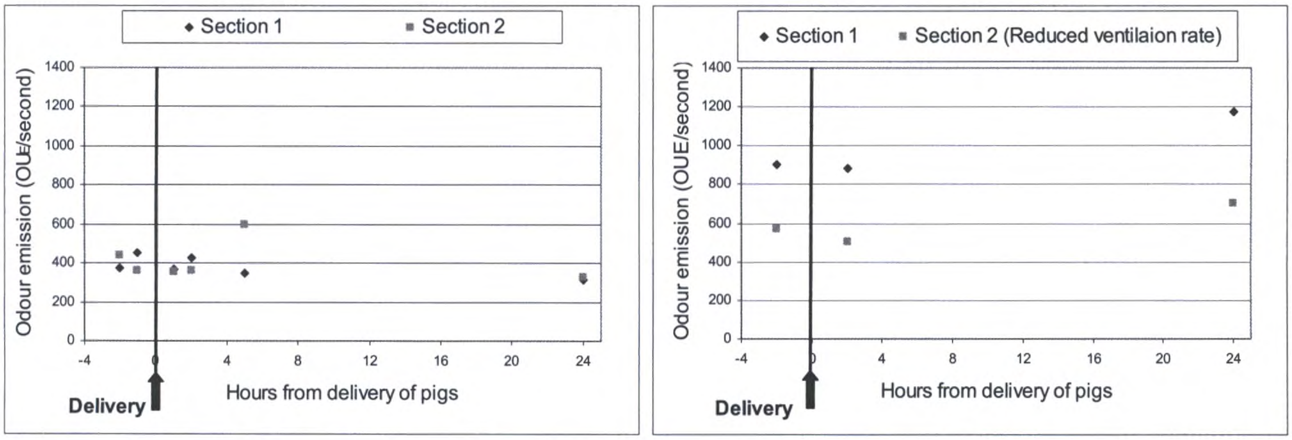


Figure 8. The odour emission from a finishing unit before and after delivery of pigs from two batches. The ventilation rate was the same before and after delivery.

Conclusions

The following conclusions can be given for the supplementary experiments:

- Odour samples can be sent by express mail to the olfactometry laboratory even if there is a risk for condensation in the bags. However, condensation is not allowed during sampling and analyzing.
- When measurements are taken in two identical sections for pigs, the variance of different odour panels can be neglected compared to the variance of the sections and the variance of the date.
- If a 50% difference in odour emission between two sections is to be demonstrated, the measurement programme could involve 10 measurement days with one single odour sample in each section, or 6 measurement days with triple odour samples in each section.

An experiment showed that odour from clean pigs can be neglected, because the odour mainly originates from the manure. This means that it is very important to maintain a good dunging behavior in units with partly slatted floors. In addition, it will mean that the odour emission from finishing units with partly slatted floors is less than from units with fully slatted floors.

The odour emission from finishing units with slurry systems is 3-5 times higher during the summer than during the winter. An experiment showed that the odour emission can be reduced by cooling the inlet air.

Management factors to control the thermal comfort for the pigs are essential, as the ventilation rate must not be too high in relation to the odour emission, and nor too low in relation to the dunging behavior.

A number of feed experiments have demonstrated reduced ammonia emission, but not reduced odour measured by olfactometry.

In the future biological filters will be a solution for the odour problems, and maybe the new membrane technology could be a solution. In Denmark, scrubbers using a solution of sulphuric acid can only be used as ammonia reduction techniques and not for odour reduction.

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Analytical Challenges in Measuring Odorant Emissions from Animal Operations

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Abstract

Accurate measurement of odorant emissions associated with animal agriculture is a challenging undertaking as accurate air concentration data is required. Quantitation of the large number of odorants associated with animal manures is difficult due to the physical/chemical properties of the analytes (highly polar, reactive and volatile), the variability of the ambient air matrix (temperature, relative humidity and dust levels), and the difficulty in creating analytical standards for quantification. Odorants fall into a number of organic compound classes, i.e., sulfides, mercaptans, amines, phenols, indoles and fatty acids, and include inorganic chemicals like hydrogen sulfide and ammonia. The large range of compound classes, polarity, reactivity and volatility require that several analytical methods be used. Many researchers working in this area have operated in an odorant identification mode only or have presented relative concentration data as a means to evaluate emissions from animal operations used to evaluate some odor control technology. In order to accurately determine emission factors for even selected odorants, some basic QA/QC principles are required to validate the effectiveness of a an analytical method. One of the most important factors in assessing the effectiveness of an odorant's analysis is to determine the effect of humidity on analyte collection efficiency and instrument performance. For highly polar analytes such as volatile fatty acids, collection efficiency on a sorbent material may be drastically decreased under high humidity conditions. In addition, recovery and analysis of polar compounds in canisters systems are also affected by ambient humidity levels. Analysis of samples with excess water from high humidity environments will lead to shifts in retention time of analytes and loss of signal intensity during analysis. Another critical issue is the development of accurate calibration curves for analyte quantitation. For example, use of permeation device to create a methyl mercaptan standard gas is complicated by the reaction in the presence of oxygen and light to form dimethyldisulfide, another important odorant. This paper will provide an overview of the current state of the science with respect to odorant analysis, including the limitations of each major approach.

Introduction

Gaseous emissions from animal operations are extremely complex mixtures of organic and inorganic chemicals from numerous compound classes. Some of these gases are relevant from a global warming perspective, i.e., methane, carbon dioxide. Others are important from an air quality perspective; for example some volatile organic chemicals (VOCs) may contribute to the formation of ground-level ozone. However, public concern over animal operations is often focused on the problem of persistent odor emissions which can create a negative physiological and/or psychological response in residents living in downwind areas.

A number of common odorants may elicit an olfactory response at concentrations in the low parts-per-billion level (Table 1). Therefore, scientists investigating these chemicals in the environment must strive to achieve very low analytical detection limits. Existing analytical methods for VOC detection were developed and validated for monitoring of industrial pollutants in urban environments at the parts-per-million levels. Volatile compounds important for agricultural air quality studies are often polar, reactive, and highly sorptive on surfaces; whereas, most validation studies for these different sampling techniques were performed on stable, non-polar hydrophobic compounds. The purpose of this paper is to provide an overview of available methods for sample collection, analysis and quantitation of odorants and to provide a description of research gaps in our critical knowledge.

Table 1. Olfactory detection thresholds for common odorants

Compound	Odor threshold (ppbv)	Compound	Odor threshold (ppbv)
Methyl Mercaptan	1.1	Acetic Acid	145
Ethyl Mercaptan	1.1	Propionic Acid	33.5
Propyl Mercaptan	1.3	Butyric Acid	3.9
Butyl Mercaptan	1.4	Isobutyric Acid	19.5
Carbon Disulfide	95.5	Valeric Acid	4.8
Dimethyl sulfide	2.2	Isovaleric Acid	64
Dimethyl disulfide	12.3	Para-cresol	1.9
Trimethyl amine	2.4		

Sample Collection

Current ambient air sampling techniques used in agricultural air quality studies typically use either a whole air (syringe, Tedlar bags, or stainless steel canisters) sampling approach or pre-concentration (sorbent tubes and solid phase microextraction [SPME] fibers) sampling approach. Each sampling approach and technique has its advantages and disadvantages, but all have one thing in common they were never developed for sampling the types of compounds and environments that are associated with animal feeding operations.

Thermal Desorption

General guidelines on the use of active sampling onto sorbent tubes are found in EPA Compendium Method TO-17 (Woolfenden and McClenny, 1997). This document discusses in detail procedures to follow for sampling and analysis along with supporting reference list. In the appendixes, there are tables listing sorbent material properties, different sorbent tube combinations, and recommendations on the types of sorbent material needed to capture specific compounds. In terms of relevance to agricultural air quality, only two of the 74 compounds listed in the back tables have been identify as agricultural odorants with an additional four compounds listed as major compounds emitted from animal feeding operations. Based on TO-17 three troubling areas emerge as needing validation in agricultural air quality studies: 1) sampling flow rates; 2) safe sampling volumes; and 3) minimizing the interference of water.

Stainless Steel Canisters

Blunden et al. (2005) recently released characterization of VOC from a swine operation using canister sampling and analysis. They determined that dominate compounds emitted from swine facilities were ethanol, methanol, acetaldehyde and acetone with most agricultural odorants never detected above 7 ppbv. These results are not surprising since Koziel et al. (2005) demonstrated that recovery of the agricultural odorants (i.e., volatile fatty acids, 4-methylphenil, 4-ethylphenol, and indole) from 6 L SUMMA canisters were less than 5% after 0.5 hour of storage and dropped to less than 1% following 24 hours of storage. Ochiai et al. (2002) has shown that increasing relative humidity levels in the canisters lowers recovery of oxygenated (alcohols) compounds. These results are as expected since canister sampling was designed for sampling VOC with vapor pressures greater than 10^{-1} torr at 25°C and 1 atm (McClenny and Holdren, 1999); whereas, many of the agricultural odorants have vapor pressures less than 10^{-1} torr resulting from their polar nature that creates large cohesive energy between molecules (Castellan, 1983) . However, new developments in fused silica lined canisters and heated inlets have the potential to extend the range compounds to include semi-volatiles (Robinson et al., 2004).

Solid Phase Microextraction

SPME has become a widely-used technique for the pre-concentration of volatile and semi-volatile organic chemicals in both liquid and gas-phase samples (Zhang and Pawliszyn, 1993, Lord and Pawliszyn, 2000, Beltran et al., 2000). SPME is a one-step extraction procedure where the compounds of interest are absorbed by a thin polymer film or by porous carbonaceous materials that are bonded to a fused silica fiber. SPME is based on an equilibrium process, and at equilibrium the mass of analyte on the fiber is proportional to its concentration in the sample matrix (Pawliszyn, 1997). This technique can also be used under non-equilibrium conditions to determine concentrations as long as the exposure time for the fiber is the same for standards and samples. This approach is especially sensitive for gas phase samples as matrix interferences are minimized versus liquid samples. Another advantage of SPME is that no pumps or mass flow meters are required during sample collection. SPME fibers can be used to sample headspace vials, Tedlar bags or canisters, or they can be used for ambient air sampling. However, the mass transfer rate of analytes into the fiber matrix is influenced by temperature and air flow rate, and adsorption can be reduced by high humidity conditions and by the presence of high concentrations of competing VOCs. In addition, there is no one SPME fiber coating that provides adequate adsorption for all odorant compound classes, and there are serious challenges in attempting to calibrate SPME fibers for quantitative analysis of gas phase samples.

Analytical Methods

Gas chromatography-mass spectrometry (GC-MS) is the most sensitive and useful analytical method available for the detection of VOCs. A 30-60-m megabore capillary column with a thick film (1 um), non-polar stationary phase is generally used to retain and efficiently separate the traditional analyte set of non-polar industrial VOCs. However, chromatographic peak shape for the more polar VOCs of interest in an animal agriculture setting, i.e., sulfides, mercaptans, amines, phenols, indoles and fatty acids, is extremely poor when using a typical "Volatiles" column. A more polar stationary phase such as Carbowax or a Porous Layer Open Tubular (PLOT) column is required to maximize separation and signal-to-noise ratios.

In many cases, odorants are small components within a complex air sample matrix containing both polar and non-polar constituents. Critical odorants may become "buried" beneath enormous co-eluting, non-odorous hydrocarbon peaks of similar volatility. Scientists have utilized a number of strategies to tease out and identify these critical odorants. A "sniffer port", or GC-olfactometry (GC-O) approach has been utilized, especially in the food and flavors industry, to monitor the effluent from a GC column using a human operator to identify chemicals which create an olfactory response and to describe the character and intensity of the odorant (Jordán et al., 2001, Ferrari et al., 2004). This approach alone, however, does not address the chromatographic peak shape problem.

The use "heart cutting" techniques or multi-dimensional GC-MS has been successfully applied to odorant analysis whereby, a preliminary separation is performed on a non-polar column. Portions of the effluent from this column are cryo-focused onto the head of a second, more polar column for further separation and analysis by mass spectrometry and sniffer port (Wright et al., 2005). While methods development for a large analyte list is challenging with MD-GC-MS, this approach does provide sufficient sensitivity and selectivity to detect polar VOCs at environmentally relevant concentrations.

Quantitation Methods

One of the most challenging aspects of odorant VOC analytical method development is detector calibration. This challenge stems from the difficulty in creating stable, traceable standard mixtures. Significant variations in chemical and physical properties of the different odorant compound classes necessitate the creation of separate standards for each group. Volatile fatty acids, for example, are created in an aqueous solution of pH <2. Amines on the other hand must be created in an alkaline solution. Some analytes are only soluble in an organic solvent which may cause significant chromatographic co-elution problems, while still others are in the gaseous state at room temperature.

Three potential approaches may be utilized in gas or liquid standard creation. High purity chemical standards may be acquired, and standard solutions may be created by the analyst. However, handling and storage of pure odorant chemicals presents potential worker safety hazards due to their generally poisonous and corrosive nature. This work may also create serious nuisance odors in a laboratory building. The use and handling of pure standards is most appropriate for those chemicals which are solids at room temperature.

For highly volatile chemicals, certified gas standard mixtures may be purchased from a few specialty companies. Since the constituents of the mixture and the proportion of the constituents within the cylinder are set, this approach is most appropriate for a routine analysis method where the sample concentration ranges and the analytes of interest are well-established. Certified gas mixtures are also costly and may have a very limited lifetime before degradation begins to occur within the cylinder.

Alternatively, certified permeation devices may be used to create standard gases. Permeation devices are generally a sealed Teflon tube containing the pure chemical. The length of the tube and the thickness of the membrane dictate the mass of chemical emitted. Permeation devices are certified at a particular temperature by monitoring the change in mass of the device over time, and this certification process may take several weeks for devices with low emission rates. These devices also require an instrument containing a thermostated chamber with accurate gas flow control through the chamber. Gas flows from several permeation chambers may be combined to create a mixed gas standard. However, precise control over dilution gas flows must be maintained, and care must be taken when mixing gas standards to avoid reactions which may create additional chemicals within the gas stream. The primary resources required for this calibration method are time and carrier gas. While some units may be able to utilize filtered laboratory air as a carrier gas, scientists may wish to use nitrogen or helium to minimize oxidation reactions of some analytes. Significant time is required to allow the chamber system and associated tubing to equilibrate when altering dilution flow or when changing to new chemicals.

Conclusions

The goal of a single standard sample collection and analysis method to evaluate odorant emissions from animal agriculture is unrealistic considering the enormous number of potential odorants emitted from any one facility. Scientists have begun to identify key odorants associated with particular animal species; however, conditions will vary widely between different facilities and between operations in different regions of the country with different climate conditions. Researchers need to approach sampling and analysis from a multifaceted perspective that considers not only the chemistry of the compounds analyzed but also the matrix in which these compounds exist. While existing methods may be effective at identifying odorants within a particular gas sample matrix, significant work remains to develop quantitative sample collection and analysis methods to accurately measure odorant concentrations under conditions typically found in animal production facilities. These methods should incorporate appropriate quality assurance and quality control procedures such as evaluation of humidity on selected adsorbent tubes with respect to breakthrough volumes. Development of these methods will only be successful if they incorporate a fundamental knowledge of the chemical properties of the analytes and of the sample matrix.

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Emissions Approaches and Uncertainties - Crop

Uncertainties in the Current Knowledge of Atmospheric Trace Gases Associated with Cropping Systems in the U.S.

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Abstract

Emissions of C- and N-derived trace gases from agriculture-related activities have a significant influence on the nation's air quality. Approximately 80 different crop species are grown in the US in widely differing geographic areas and climatic conditions. Other crop growth regulating factors consist of differences in soil types, moisture availability, nutrients and management practices. The crops grown include both C3 and C4 species, and a multitude of cultivars. Although the majority of cultivated acreage in the US is planted with only about ten major crop species, uncertainties associated with trace gas emissions arise from: (1) limited data availability and consequently inaccurate estimates due to the large temporal and spatial variability in trace gas (principally CO_2, CH_4, NH_3 and N_2O) composition and amounts released from agricultural activities, (2) characteristics of pollutant emissions from animal feed-lots (including emissions from dairy animals) and their geographic distribution and (3) our limited understanding of semi-volatile organic compounds (SVOCs) associated with agriculture. SVOCs range in their composition from relatively simple acids to complex organo-chlorines and pesticides. These compounds exist in both particle (solid and liquid) and gas phases, with a highly variable rate of transition from one phase to the other, as governed by their chemical structure, receptor characteristics and by environmental factors.

While emission issues are of concern, so is atmospheric wet and dry deposition of N, mineral nutrients and organic compounds to cropping systems that can, in turn, have feedback effects on trace gas emissions. There are many gaps in our understanding of these processes. At present, a number of research groups are investigating agriculture-related emissions of trace gases (primarily CO_2, CH_4, NH_3 and N_2O). However, there are advantages and limitations associated with the various methodologies used for quantifying emissions and deposition (e.g., flux measurements, use of continuous monitoring versus passive sampling of the air, sample collection and chemical analyses). There is also a frequent lack of sufficient number of monitoring sites (sample size) to satisfy the requirements of spatial mapping of the measured variable with confidence. Other considerations include: (1) the effects of increasing concentrations of atmospheric O_3 and CO_2 on crop production, and the potential changes in management practices of cropping systems, (2) the changing use of N fertilizers in agriculture and consequent alterations in atmospheric NO_x , N_2O and NH_3 emissions and deposition, and (3) changing air temperature effects on crop production and also its impacts on trace gas emissions, particularly molecules other than CO_2. Overall, studies are needed at various scales with better-coordinated approaches to sufficiently quantify temporal and spatial trends in trace gas emissions and deposition and their relationships to agricultural practices in the US, in a changing global climate.

Nitrous Oxide Emissions in the Northern Great Plains as Influenced by Cropping Systems and N Fertility

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Abstract

Nitrous oxide is a powerful greenhouse gas and contributes to degradation of ozone in the atmosphere. Although agriculture has been identified by the Intergovernmental Panel on Climate Change (IPCC) as the major anthropogenic source of N_2O emissions, field measurements of N_2O are limited for agricultural systems, particularly in the semi-arid Northern Great Plains (NGP) region. This study was undertaken to learn more about N_2O seasonal emission patterns and levels from two-year cropping systems adapted for the Northern Great Plains, and to determine if the IPCC methodology for estimating fertilizer N induced N_2O losses is accurate for this region. Three no-till (NT) cropping systems (fallow-wheat, wheat-wheat, pea-wheat), one conventional till (CT) system (fallow-wheat) with varying N fertility regimes and one perennial grass system (no fertilizer N applied) were sampled throughout the year using static chambers. Emission losses ranged from 169 to 1115 g N_2O-N ha^{-1} for the sampling period (22-March 2004 to 2-Feb 2006). Losses were greatest from the wheat-wheat rotations because of additional N fertilizer inputs. Inclusion of a legume in the rotation did not elevate emissions beyond that observed in wheat-fallow systems. Tillage did not greatly impact losses of N_2O for the wheat-fallow systems (NT vs. CT). Emissions were episodic in nature though overall N_2O emission activity was greatest during two distinct periods. The first period (10-wk) occurs immediately after application of N. The second period occurs during the winter when soil water-filled pore space exceeded 90%. These periods collectively accounted for 69 to 94% of total emissions. Fertilizer induced emissions of N_2O ranged from 0.08 to 0.13% of applied N in 2004, to 0.51% of applied N in 2005. These emission rates are considerably below the IPCC 1.25% default value, and indicate that IPCC methodology greatly overestimates emissions for the Northern Great Plains.

Introduction

In recent years there has been an increased concern about the build-up of CO_2 and trace greenhouse gases in the atmosphere. Nitrous oxide is one trace gas that has drawn particular attention because it is a potent greenhouse gas that is estimated to have a global warming potential 270 times that of CO_2 (Duxbury et al., 1993). In addition, it has been implicated in the destruction of the ozone layer. Nitrous oxide is emitted from both anthropogenic and natural sources. Although global estimates of N_2O emissions are quite variable, agriculture has been identified by the Intergovernmental Panel on Climate Change (IPCC) as the major (77%) contributor (Kroeze et al., 1999) to anthropogenic emissions.

Current IPCC methodology assumes 1.25% (referred to as the IPCC "default value") of all N inputs from commercial fertilizer, animal manure, decomposition of plant residues, and biological N fixation is lost directly as N_2O. This default value is applied uniformly to all regions, even though climates and production practices may differ. Given that N_2O emissions are known to be affected by a multitude of environmental factors (e.g. precipitation, temperature, soil physical properties, and soil N and C pools) and management practices (e.g. cropping sequences, tillage, N fertilization rates) it seems likely there will be strong regional biases in the fraction of applied N lost as N_2O. Current research in the semiarid Canadian prairies indicates that IPCC methodology may greatly overestimate actual N_2O emissions (Lemke and McConkey, 2000; Lemke et al. 2003) from commercial fertilizer and biological N fixation (Rochette and Janzen, 2005). Comparatively little information exists on N_2O emissions from neighboring regions in the United States, and it is not known whether the current IPCC methodology (IPCC, 1997) accurately applies to this region.

This study was undertaken to learn more about emission levels of N_2O from several cropping systems adapted for the semi-arid Northern Great Plains of the United States. It is part of a larger, ongoing study that examines the impact of best management practices (BMP), including no-till and continuous cropping, on C sequestration. The work being done on N_2O is being integrated with the studies on C sequestration to provide a more complete analysis of the effect of BMP in our region on greenhouse gases balances. The objective of this presentation will be to i) illustrate seasonal patterns of N_2O emissions and periods of peak losses in several cropping systems; 2) estimate total season losses of N_2O and fertilizer induced losses of N_2O under these cropping systems; and 3) contrast field-measured losses of N_2O against predicted N_2O losses using IPCC methodology.

Methods

Nitrous oxide emission data reported here were collected from a long term cropping system being conducted at the Montana State University- Post Research Farm near Bozeman. The soil at the study site is classified as an Amsterdam silt loam (fine-silty, mixed, superactive, frigid Typic Haplustolls) with 8% sand, 65% silt, 27% clay, pH 8, and 2% organic matter in the surface 30-cm. The study consists of nine cropping systems (only 4 cropping systems will be mentioned here) main-plots (24.4 x 7.4 m) replicated four times in a random complete block design (Table 1). The site was managed as a single-phase cropping system study with only one phase of the rotation occurring in any one season. Treatments were divided into sub-plots representing moderate N, and high N fertility, plus an unfertilized 0 N control. Fertilizer N, in addition to starter N applications, was applied only during phases of the rotation where wheat was grown. The moderate and high N fertility rates were determined from spring soil samples to a 60-cm depth in 2004 and 2005. The fertilizer N rates were adjusted to provide 100 and 200 kg ha^{-1} available N (soil NO_3-N + fertilizer N), respectively. Soil NO_3-N levels were determined in all sub-plots during the spring using established procedures (Mulvaney, 1996). During the 2004 season, fertilizer N was surface broadcast applied as urea to the winter wheat sub-plots on 13-April. Seeding of winter wheat occurred in September of the previous year (2003). In 2005, fertilizer N was band applied as urea to spring wheat at seeding (14-April). In 2006, winter wheat was seeded 30-September, 2005 and fertilizer N was band applied as urea. In all cases direct-seeding equipment with disc-openers for minimal disturbance was used to seed plot areas. Conventional tillage was performed in Treatment 1 with discs and cultivators equipped with sweeps.

Table 1. Treatment description at the long-term cropping systems study. Bozeman. MT.

Trt #	Cropping Sequence (2004-2005)
1	winter wheat – fallow (conventional tillage)
2	winter wheat – fallow (no-till)
3	winter wheat – spring wheat (no-till) ¶
4	winter wheat - spring pea (grain)(no-till)
5	perennial grass and alfalfa to mimic CRP

¶ winter wheat – seeded in the September, 2005

Gas sampling was conducted using vented chamber techniques (Hutchinson and Mosier, 1981). The chambers were made of plexi-glass with insulated tops. Chambers covered 1000 cm^2 of soil surface and were placed between crop rows. Gas sample collection followed the accepted protocols of Lemke et al. (1998). Samples were collected from the head space during the early to mid-afternoon (13:00-15:00 h). Air-temperatures inside the chambers and below the soil surface (2.5 cm-depth) were recorded continuously with Onset (Onset Computer Corporation, Bourne, MA) temperature sensors and data-loggers. Soil cores (0-10 cm) were collected at all sampling events to determine volumetric water content and water-filled pore space. Gas samples from the headspace were collected with a 25 mL syringe and then transferred to pre-evacuated 13 ml exetainers. The concentration of N_2O in the exetainer was determined using a gas chromatograph equipped with a ^{63}NI electron capture detector. Nitrous oxide flux was estimated from the concentration change in the chamber headspace over a 60 min. collection period as described by Nyborg et al. (1997). Briefly, changes in concentration over time were assumed to be linear and were calculated by subtracting the time-zero (or background) concentration from the final concentration. Time-zero concentrations were calculated using the approach of Anthony et al. (1995). A series of ambient air samples was collected at each sampling event. The mean of these samples was used as the time-zero concentration.

Results and Discussion

Precipitation

Annual precipitation amounts at the study site were close to the long-term averages for the two years. The distribution of precipitation by month followed the long-term norms during 2004 (Figure 1). Weather in 2005 was characterized by above normal precipitation in April, Oct., Nov. and Dec, and below normal precipitation in May.

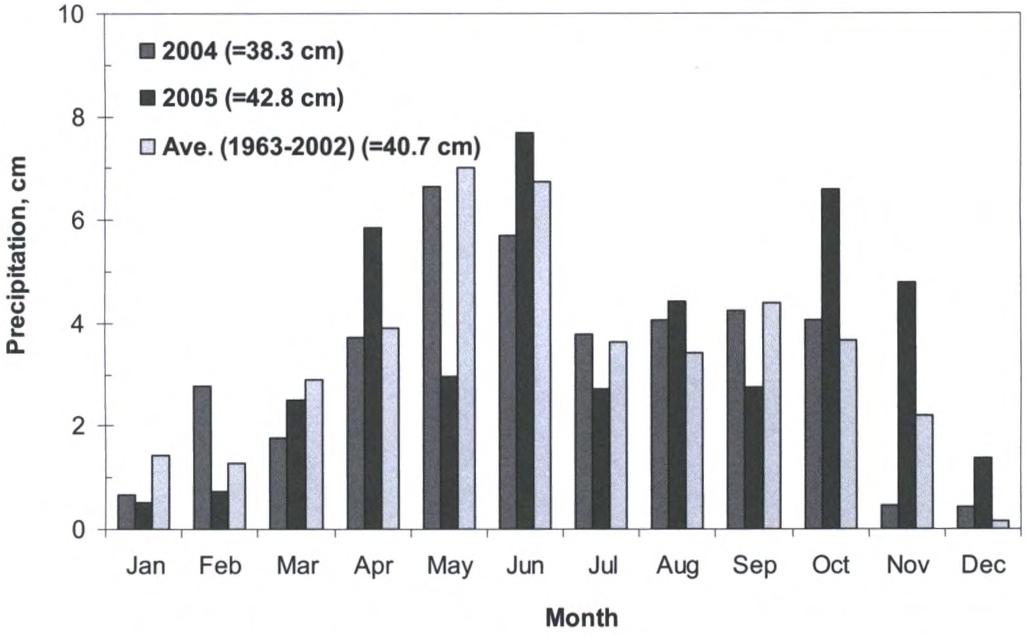

Figure 1. Precipitation amounts and patterns at the study site, Bozeman, MT

Emission Profiles

Gas sampling was initiated in late-March 2004 and has continued through the present. Nitrous oxide emission profiles for this measured sampling period (March 2004-February 2006) are summarized by Figures 2-5 for the four cropping systems. In general, the greatest emission activity occurs over two distinct periods. The first period follows application of fertilizer N, or urea and lasts approximately 10 weeks for spring application events. During this period, emission activity is elevated above ambient levels and peaks approximately two to three weeks following the fertilization event. For fertilizer urea applied in the fall (i.e. 30-Sept, 2005) elevated emission activity lasted well into the early winter months. The second period occurs during the winter or at winter thaw events. Overall, emission activity was enhanced by N fertilization. Tillage (CT vs. NT) did not greatly impact emissions for wheat-fallow systems except during the winter thaw (2-wk period) and immediately following tillage events in the summer (< 1 week/tillage event). Cropping intensity affected emissions only to the extent that fertilizer N was applied. Wheat-pea rotations produced lower emissions ($P < 0.05$) than wheat-wheat in 2005, as peas were not fertilized with N in the second year of the rotation. Inclusion of legumes in rotation did not result in elevated emissions ($P > 0.05$) compared to fallow systems either during the growing season, or following harvest.

Elevated N_2O emission activity following N fertilization was believed to result primarily from nitrification of fertilizer N. Soil moisture contents at the field site were typically below 70% water-filled pore space, and outside the water content range where denitrification processes predominate. In addition, N_2O emission activity following application of urea and KNO_3 were compared at this field site in a related study. The results demonstrated that N_2O emission activity was relatively low following application of KNO_3 in contrast to urea (data not presented). During the winter denitrification processes may be occurring in addition to nitrification as soil water-filled pore space was >90% during thawing events. This occurred in late February to early March in 2005, and during the winter of 2005-2006. The importance of winter emissions may have been enhanced by application of N fertilizer in the fall.

Estimated N_2O Losses

Estimated losses of N_2O for the examined cropping systems were generally modest in scale, ranging from 169 to 1115 g N ha^{-1} for the 22 month sampling period. Nitrous oxide emissions significantly exceeded those observed from the perennial grass system (or CRP) for only the fertilized wheat-wheat system (Table 2). The fertilized wheat-wheat exhibited the highest emission losses due to additional N inputs needed over the full cropping sequence. The two primary periods of N_2O emissions, i.e. post-N application and winter, accounted for 69 to 94% of total emissions over the 22 month sampling period. Winter emissions for unfertilized plots ranged from 30 to 42% of total sequence emissions, while winter emissions for fertilized treatments accounted for 48 to 61% of total sequence emissions. Winter emissions were much greater in 2005-2006 than 2004-2005 due to the combination of fall fertilization and an early snowfall event which prevented the soil (0-10 cm) from freezing. The potential for observing high emissions during the winter, where soils remain unfrozen, highlights the importance of fall fertilization in determining N_2O losses from cropping systems. Overall, our results suggest that new crop management strategies for the Northern Great Plains, such as no-till and inclusion of legumes in cropping systems, are secondary in importance to N fertilizer management practices such as N fertilization rate, timing (fall vs. spring) and methods of application (band vs. broadcast).

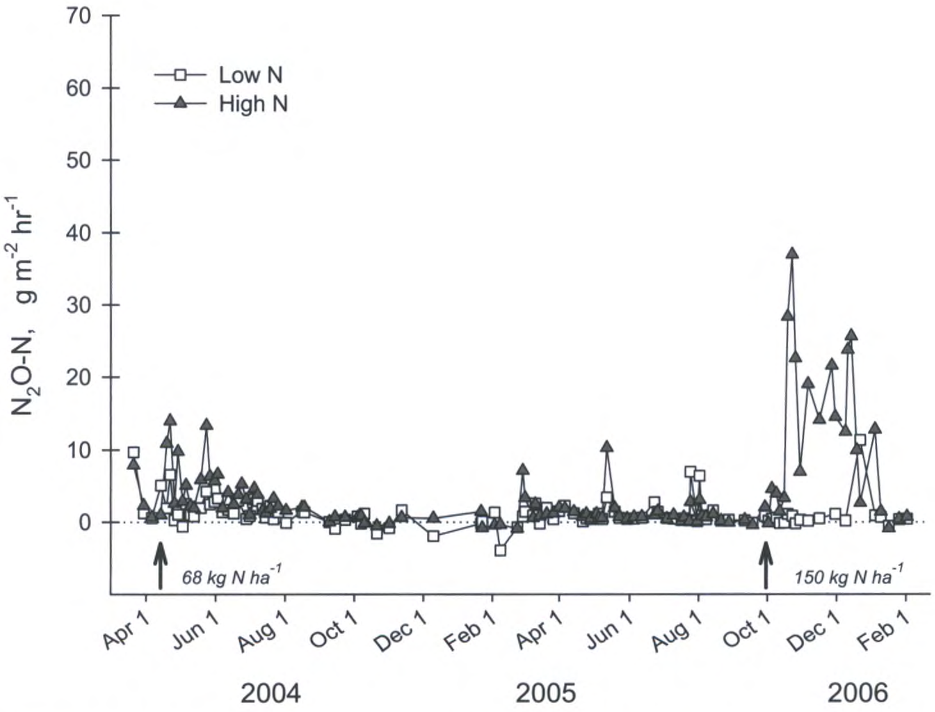

Figure 2. Nitrous oxide emission profiles over a winter wheat – fallow (CT) rotation at two levels of N fertility (low=no fertilizer, high = 200 kg ha^{-1} available N). Arrows indicate date of fertilizer N application. Bozeman, MT. Mean of four reps.

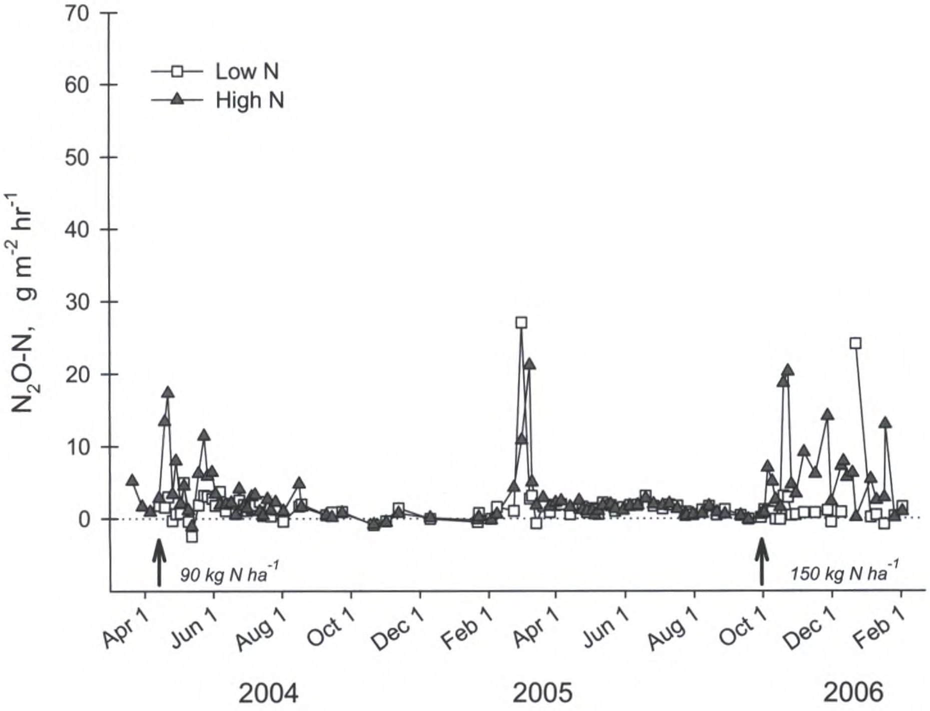

Figure 3. Nitrous oxide emission profiles over a winter wheat – fallow (no-till) rotation at two levels of N fertility (low=no fertilizer, high = 200 kg ha^{-1} available N). Arrows indicate date of fertilizer N application. Bozeman, MT. Mean of four reps.

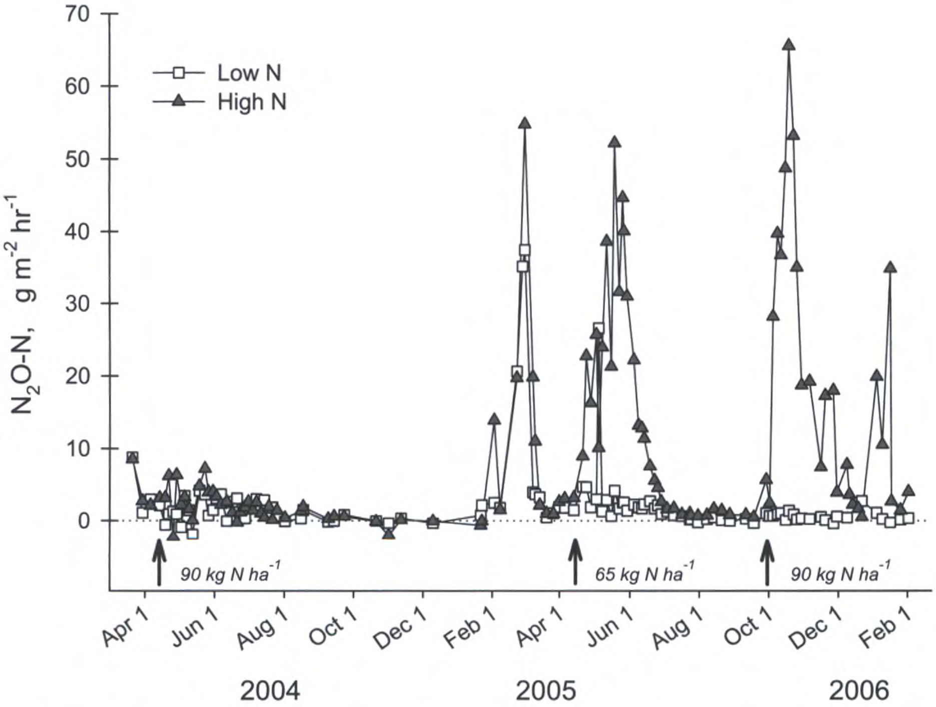

Figure 4. Nitrous oxide emission profiles over a winter wheat – spring wheat (no-till) rotation at two levels of N fertility (low=no fertilizer N; high = 200 kg ha^{-1} available N). Arrows indicate date of fertilizer N application. Bozeman, MT. Mean of four reps.

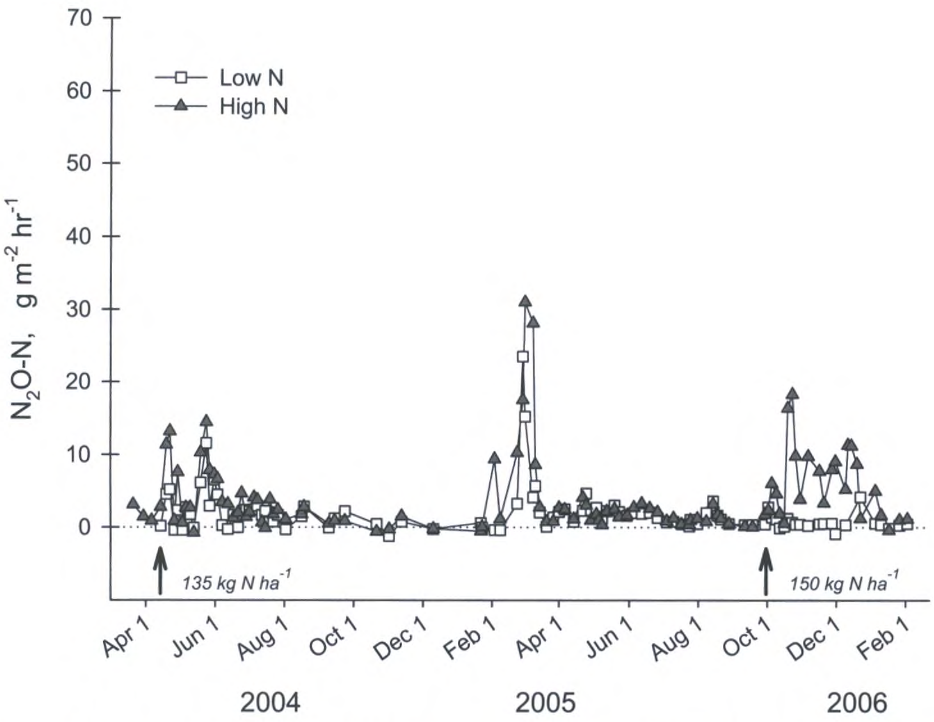

Figure 5. Nitrous oxide emission profiles over a winter wheat – spring pea (no-till) rotation at two levels of N fertility (low=no fertilizer N high = 200 kg ha^{-1} available N). Arrows indicate date of fertilizer N application. Bozeman, MT. Mean of four reps.

Table 2. Estimated losses of N_2O during the 10-week period following N fertilization (% season total) and full season (22-March, 2004 to 2-February, 2006).

Trt#	Cropping system	N level (no. of N application events over 22 months)	Emission levels		
			10 wks post N application	Winter	Total
			g N_2O-N ha^{-1} (% of total)		
1	w. wheat-fallow (CT)	low (0)	62 (38.5)	64 (30.6)	169
1	w. wheat-fallow (CT)	high (2)	127 (26.3)	327 (60.6)	518
2	w. wheat-fallow (no till)	low(0)	62 (31.1)	134 (42.2)	250
2	w. wheat-fallow (no till	high (2)	120 (29.6)	225 (53.5)	414
3	w. wheat-s. wheat (no till)	low (0)	92 (43.2)	107 (40.6)	235
3	w. wheat-s. wheat (no till)	high (3)	428 (46.4)	633 (47.6)	1115
4	w. wheat – s. pea (no till)	low (0)	88 (39.1)	68 (29.7)	225
4	w. wheat – s. pea (no till)	high (2)	140 (28.7)	271 (55.4)	487
5	perennial grass or CRP	low (0)	77 (35.2)	87 (37.2)	227
	LSD (0.05)		60	310	325

Fertilizer Induced Emissions

We calculated the fraction of fertilizer N lost as N_2O in 2004 and 2005 based on our estimates of total losses observed from 13-April 2004 to 13-April 2005, and 14-April 2005 to 2-Februrary, 2006, respectively. Nitrous oxide losses from treatments not receiving fertilizer N were considered background levels. These levels were subtracted from estimated N_2O losses for the high N treatments, yielding "fertilizer induced" losses. These losses were expressed as a percentage of the total N applied and the results are presented in Table 3. Our results indicate that for all cropping systems, fertilizer N induced emissions in 2004 were well below the IPCC default value of 1.25%. Losses ranged from 0.09 to 0.13% of fertilizer N, or more than one order of magnitude lower than the IPCC default value. In 2005, fertilizer N was only applied to the continuous wheat system (Trt 3). Estimated fertilizer induced losses of N_2O (i.e. 0.50%) were much greater during this season but still below the IPCC default value. These results suggest that IPCC default methodology will greatly overestimate N_2O emissions for the semi-arid Northern Great Plains region.

For the continuous wheat systems, the large difference in fertilizer induced losses of N_2O between the two years may have been the result of two factors. First, differences in fertilizer N placement strategies may have impacted N_2O emissions. Fertilizer N was applied to spring wheat at seeding in a subsurface band (2005), while fertilizer N was surface broadcast applied to winter wheat in 2004. Though direct comparisons between band and surface applications of fertilizer N in the field are limited, laboratory studies by Tenuta and Beachamp (2000) found relatively high concentrations of urea placed in small volumes of soils increased the fraction of N lost as N_2O. The second factor that may have impacted losses is the level of competition between plants and microbes for NH_4 derived from fertilizer N. Although, microbes have traditionally been viewed as superior competitor for this N (Rosswall, 1982), it is curious that fertilizer N applied to an actively growing winter wheat crop in the spring (i.e. 2004) resulted in substantially lower emission peaks than when N was applied to wheat at seeding (2005, both spring and fall).

Table 3. Estimated fertilizer N-induced N_2O emissions for four cropping systems.

Trt	Cropping system	2004†		2005‡	
		g ha^{-1}	%	g ha^{-1}	%
1	w. wheat-fallow (CT)	88	0.13	-	-
2	w. wheat-fallow (no till)	70	0.08	-	-
3	w. wheat-s. wheat (no till)	97	0.11	333	0.51
4	w. wheat–s. pea (no till)	124	0.09	-	-

† 2004 period = 14-April, 2004 to 14-April, 2005

‡ 2005 period = 15-April, 2005 to 30-Sept, 2005. Fertilizer N was not applied to fallow and peas in 2005.

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Aerosol Emissions from Field Planting Operations

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Abstract

Dust plumes generated by agricultural field preparation and planting operations were measured remotely via aerosol lidar and sampled with a variety of aerosol point samplers in order to generate plume space and time dynamics, quantify aerosol concentrations and determine the chemical composition of generated dust. Particle number and mass distributions measured from two cotton operations (disking, harvesting) in a flood irrigated field in New Mexico indicate approximately 45-50% of the measured mass was $PM_{2.5}$ and 85-95% was PM_{10}. Plume dynamics and local wind condition interactions were quantified and visualizations from the lidar measurements are shown.

Introduction

Agriculture is under increased scrutiny as a source of airborne particulate matter and the relative lack of research documenting the emissions of fine ($PM_{2.5}$) and coarse (PM_{10}) particulate matter from agricultural operations leads to uncertainty in agriculture's contributions. Previous studies that quantified agricultural emissions represent a very limited number of sites, a low number of replicate samples, and few early studies quantified $PM_{10.}$ Instead, total suspended particulate (TSP) matter or industrial workplace respirable dust (PM_4) was measured. The application of lidar remote sensing techniques to PM emission factor measurements is relatively new (Holmén et al., 1998, 2000a,b). Lidar techniques help overcome one of the major limitations of point sampling methods; namely, the uncertainty in determining the dust plume height over which to integrate modeled PM concentrations. Previous field investigations resulted in a framework for categorizing vertical PM_{10} profiles and an emission factor quality rating system (Holmén et al., 2000a,b). To our knowledge, no previous studies have quantified the particle size distributions and plume dynamics of agriculturally-derived field preparation and harvesting operations.

The overall objectives of this research are to use the joint capabilities of the lidar and point samplers to quantify emission factors from different agricultural operations. In this paper, the point sampler particle size distribution and lidar spatial statistics data for fugitive dust emitted during two cotton operations – disking and harvesting – are used to further refine the sampling and data analysis methodologies for agricultural $PM_{2.5}$ emissions estimation.

Methods

Site and General Cotton Operations

Field measurements were made at two ~ 2.8 ha flood irrigated experimental cotton fields located at the New Mexico State University Leyendecker Plant Science Research Center (lat. 32.2° N; Long. 106.8° W; elev. 1180 m). Experimental Field 1 was used to measure dust emissions from the field disking on 3/31/05. Field 2 was used to measure the dust emissions from upland 1517 BT cotton harvesting (11/7/05). Both the fields were a mixture of Armijo clay loam and Harkey loam soil types (USDA, 2005). An automated weather station continuously recorded hourly averages of precipitation, solar radiation, wind speed and direction, temperature and relative humidity. A Campbell Scientific three-axis sonic anemometer mounted on a tripod 1.5 meters above the ground measured air temperature (T), virtual air temperature (Tv) and the streamwise (u), cross-stream (v) and vertical (w) wind components at 20 Hz sample rates.

Dust Emissions Measurement Procedures

Dust emissions were measured simultaneously by point samplers located in the field and also remotely sensed by a LIDAR located 600 m south of the field. Sampling was conducted in replicate for one-way field passes of the implement; sampling began prior to tractor engine start and continued until several minutes after the tractor turned off its engine (when the generated dust plume moved out of the sampling area). The total number of passes sampled for disking and harvesting were 26 and 18. Point samplers were mounted on the 3-point hitch of a second tractor positioned near the center of the field, 2 to 5 rows downwind (4 to 7 meters from the nearest operation row) from the pass path (Figure 1a). After each pass the samplers were relocated to maintain a constant distance from the implement during the various replicate passes.

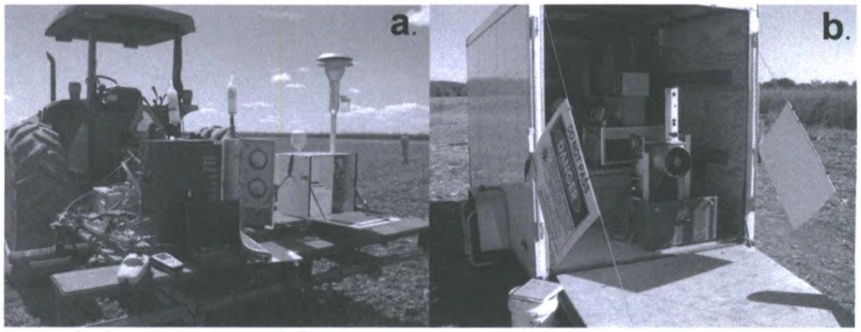

Figure 1. (a) Cascade impactors and PM samplers mounted on second tractor positioned in the field downwind of the operation; (b) UCONN scanning elastic-backscatter aerosol lidar in the field trailer

Point Particulate Matter Instrumentation

Five point PM samplers were used in the field to measure particle number and mass concentrations. An electrical low pressure impactor (ELPI, Dekati LTD., Finland) operating at 30 LPM measured particle number distributions (7 nm – 8 μm) in real time with 1-2 second resolution. Samples of particulate matter collected on aluminum foil substrates were also used for chemical analysis. A micro-orifice uniform deposit impactor (MOUDI; Model 110, MSP Corporation, Shoreview, MN) was used to collect time-integrated particle size distribution (56 nm to 18 μm in 10 stages) for mass and chemical analysis on 47 mm aluminum foil substrates and a 37 mm Teflon after-filter. A PQ200 sampler (BGI Inc. Waltham, MA) outfitted with the Very Sharp Cut Cyclone was used to collect $PM_{2.5}$ at 16.7 LPM on 47 mm Teflon membrane filters. Two GT-640A particulate monitors (Met One Instruments, Inc., Grants Pass, OR) were used to characterize the 1-min real-time mass concentrations of total suspended particles (TSP) and PM_{10}. The monitors operate at 4 LPM and the measurements are performed using a forward light scattering detector and a built-in data logger.

Lidar Measurements

Dust cloud size, shape and movement were measured remotely via the University of Connecticut portable scanning backscatter elastic lidar (wavelength 1064nm, 125mJ/pulse, 17ns (2.55m) range resolution) (Hiscox et al., 2006). For the disking operation, a series of horizontal scans was designed to sample the entire plume starting at an elevation just above the field and successive scans were collected at increasing elevations. A single lidar sampling sequence, consisting of 5 to 15 different elevation angles, was collected in less than one minute and was repeated 5 to 10 times for each pass depending on the dust's persistence in various meteorological conditions. A similar sequence was used for the harvesting operation, with the addition of a series of vertical scans moving across the field on every fourth pass of the tractor. Each scan was combined in lidar data analysis software to characterize the three dimensional dust plume on this time scale.

Results

Particle Number and Mass Distributions

The ELPI and MOUDI impactor number- and mass-based size distributions were averaged and compared for the disking and harvesting operations (Figure 2). Both the number and mass-weighted distributions indicate multimodal distributions for both operations. Number distributions displayed two modes for both disking and harvesting: in the ELPI filter stage (7 – 29 nm) and the 1.6 to 2.4 μm diameter stage (Figure 2a). Mass distribution modes were observed in the 320 nm and 5.6 μm diameter MOUDI stages for disking and the 180 nm, 560 nm and 10 μm diameter MOUDI stages for harvesting (Figure 2b). The measured mass emissions were higher for harvesting than for disking for most MOUDI stages. To some extent this reflects the higher observed background signals during harvesting due to activity on nearby fields. Fine particulate matter ($PM_{2.5}$) represented 51 and 45% of the total mass measured by MOUDI for disking and harvesting, respectively. Coarse particulate matter (PM_{10}) represented 96 and 83% of the total mass measured by MOUDI for disking and harvesting, respectively.

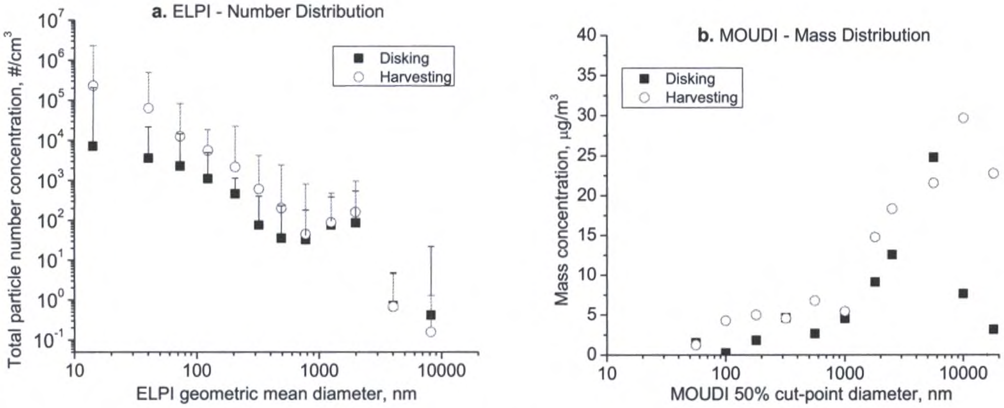

Figure 2. ELPI (a) and MOUDI (b) particle number and mass distributions for disking and harvesting operations

Lidar Detection of Dust Plumes

All lidar returns were combined to give 2-dimensional contour maps of relative density after raw signal background-subtraction and range-correction. Each map was examined visually to identify the dust plume as well as possible interference (dust/spray from offsite fields) that could affect further analysis. Overall, 20 of the 26 disking passes and 10 of the 11 horizontal harvesting passes were classified as valid. To determine dimensional information about the dust plume, an edge value, defined as 20% of the peak return value, was used to isolate the dust plume from the surrounding area. Plume area was quantified and plotted versus height. Plume areas and peak concentration values decreased with height, as expected for a ground-based source. Plume velocity, defined by the movement of the peak concentration values in space over time, indicated detectable plumes within the lidar field of view for at least 10 minutes after some passes. Plume movement was found to correspond with the mean wind direction during each pass. The detectability, plume velocity, size and intensity varied with meteorological conditions. For example as stability increased, the height of the detectable plume decreased. An example of the detectable plume for a single pass of the tractor is shown in Figure 3.

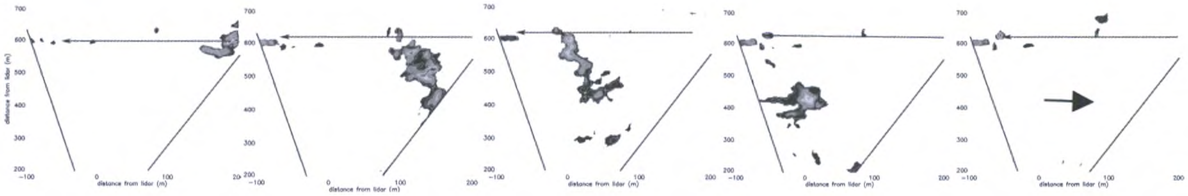

Figure 3. Sequence of lowest elevation angle lidar images from pass 8 of the tractor (disking operation). Each panel is 1 minute and 13 seconds in duration. The tractor moved from right to left across each image at a distance of 600 meters from the lidar (the horizontal line near the top of each panel approximates tractor path). The tractor pass was completed and the tractor was stopped between the last two images. The structure visible in the last image is the tractor itself. The wind direction for this pass was 319 degrees from north and is indicated by the arrow in the last panel. The lidar aim was approximately 47 degrees off of true north.

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In Field Assessments of Dust Generation of Harvesting Equipment

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Abstract

In tree nut production, the harvesting operation, consisting of removal and separation of the nuts from orchard debris, is recognized as one of the most intensive dust generation activities in crop production. The majority of US nut production, primarily almonds and walnuts, is located in the Central Valley of California, a US EPA non-attainment area for PM in ambient air. Peak levels of ambient particulate concentrations coincide with the peak agricultural harvest season. This project investigated dust generation from tree nut harvesting, specifically the "pick up" operation in which windrowed orchard material is mechanically lifted into a mobile air separation chamber where soil and other debris are removed from the nuts. While long term industrial efforts are addressing redesign of the nut handling machinery, the hypothesis in this project was that operation of existing machinery could be adjusted to reduce dust discharge and that grower-controlled factors such as ground speed and orchard surface preparation could be manipulated to reduce emissions. Particular challenges in investigating in-field processes with significant numbers of variables are the constraints on the number of analytical samples that can be processed and the time delay between sample collection and availability of data. For grower outreach activities and to provide immediate feedback on efficacy of operational changes and to allow simultaneous sampling at multiple sites, rapid, low-cost instrumentation is required. This project used industrial opacity measurement systems mounted in-situ on harvesting equipment and positioned in orchards to determine relative effects of operational changes on potential dust generation. During the 2005 harvest season, the effects of simple operational changes in the harvester equipment, e.g., ground speed, rotational speed of the nut/debris nut separation fan and preparation method for the orchard windrow. Based on air opacity measurements, intensity of dust generation could be reduced by harvesting at lower ground speeds, operating the equipment with lower air velocity and by proper adjustment of windrowing machinery. The immediate availability of data allowed in-field grower education and outreach activities. The monitoring system developed for this on-going study can be used to establish benefits of differences in machine design, harvester operating conditions and orchard management practices. The results from this tool can be used for immediate feedback on potential dust intensity based on soil conditions, soil types, harvester type and harvester operating conditions.

Concentrations of Current-Use Agricultural Pesticides in the Air, Yakima County, Washington

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Abstract

Concentrations of some of the current-use pesticides have been measured in air in many locations throughout the world, but relatively few measurements have been made in irrigated, arid regions. During the 2003 growing season, weekly integrated air concentrations (vapor and particulate phases) of 50 pesticides and selected transformation products were measured at a sampling site in Yakima County in south-central Washington State (about 20 cm/yr of rainfall). The dominant agricultural crops in this area include orchards, corn, alfalfa, and grapes. These are protected by a large number of insecticides, fungicides, and herbicides. The most commonly detected insecticides were carbaryl (100% detection), permethrin (100%), and malathion (57%). Myclobutanil (95%) and metalaxyl (76%) were the most commonly detected fungicides, whereas dacthal (95%), trifluralin (62%), and acetochlor (62%) were the most commonly detected herbicides. Of the 50 target pesticide compounds, 41 of them were detected in the air at least once. No simple relation was observed between pesticide detection frequencies and the application rate in the surrounding area (160 km^2), their use rank in the surrounding area, their mean air concentrations, or their vapor pressures. All frequently detected compounds were used substantially in 2003 in the surrounding area except for dacthal. Dacthal was used on various crops in parts of south-central Washington and likely was transported through the air to the sampling site. Seasonal variation in the total concentrations for many of the insecticides detected in the air was highest in the spring and late summer, whereas, fungicide and herbicide concentrations were more consistent throughout the growing season. Carbaryl, used extensively in the spring and autumn on orchards in this area, had the highest measured concentrations among the target compounds (280 ng/m^3 in one September air sample).

Introduction

As the population grows, there is a greater need for agricultural products. This has led to increased use of pesticides to increase yields. A fraction of the pesticides applied to agricultural fields are transported away from their intended target and can contaminate both water and air. Pesticides enter the atmosphere either through volatilization, wind erosion, or spray drift; pesticides can be removed by wet (rain, snow) and dry (dry fall, vapor partitioning) depositional processes or through photochemical reactions. Atmospheric transport (both short range and long range) has been shown to be an important factor in the transport of pesticides through the hydrologic system (Majewski and Capel, 1995; Shen et al., 2005). There have been a number of local and regional-scale studies that have frequently observed pesticides in the atmosphere (Majewski and Capel, 1995; Majewski et al., 1998; Foreman et al., 2000; Kuang et al., 2003; Peck and Hornbuckle, 2005). There have been very few studies of pesticides in the air in arid regions. This study is the first to report ambient air concentrations of current-use pesticides in Washington. There have been short-term studies of the pesticides 2,4-D, parathion, and methamidophos in the air during and after their application in Washington (Ramaprasad et al., 2004; Reisinger and Robinson, 1976; Batchelor and Walker, 1954) This area provides an interesting environment for studying pesticides in the air, since it is quite arid and is an intensely agricultural area that uses a number of different of insecticides, fungicides, and herbicides on a wide variety of crops.

Methods

The Granger Drain basin, a 5.5 km^2 watershed within the Yakima River Basin in Washington, is an agriculturally intense area (Payne et al., 2006). Eighty-seven percent of the watershed area is used for crops and rangeland/pasture. Twenty-eight percent of total area is used for orchards. Corn, alfalfa, and grapes are the next largest crops by land area (22%, 9%, and 8%, respectively). This area receives only about 20 cm/yr of annual rainfall, mostly in isolated thunderstorms. There are a wide variety of pesticides used in this area to control weeds and insects (Table 1).

Air sampling was conducted from April to September 2003 and again in May 2004 with two samplers. A high-volume air sampler (flow rate of 476 L/min) used one glass-fiber filter to collect particle-associated pesticides followed by two cleaned, polyurethane foam plugs (PUFs) to collect vapor-phase pesticides. A low-volume air sampler (flow rate of 198 L/min), equipped with a pre-weighed glass-fiber filter, collected total suspended particles (TSP). A total of 21 samples were collected. Between sampling and analysis, the PUFs and filters were stored in a freezer. The PUFs and filters for pesticide analysis were individually extracted in a Soxhlet apparatus with a mixture of 70/30 (v/v) hexane/ethyl acetate. The solvent volume was reduced in a Kuderna-Danish apparatus to about 15 mL and then, further reduced to less than 100 μL by a stream of purified nitrogen. The samples were analyzed with a gas chromatograph / mass spectrometer in selective ion monitoring mode. The target chemicals are given in Table 1. All blanks showed no contamination greater than the minimum detection limit. Recoveries of the analytical surrogate, butachlor, were 60 ± 38% (N=68). None of the sample data was adjusted according to surrogate recovery. It has been observed that carbaryl degrades to 1-napthol in the detector, but no corrections were made for the concentrations of either compound in these results. After sampling, the pre-weighed, TSP filters were placed in a desiccator to dry until they reached a constant mass and then weighed again on an analytical balanced. Further sampling and analysis details can be found in Ohrt (2005).

Results and Discussion

Fifty pesticides and pesticide transformation products were targeted in this study (Table 1). All but nine of these compounds were observed at least once during the study. At least 3 of the 50 target chemicals were detected in every air sample including carbaryl and trans-permethrin, which were detected in every sample. Of the 22 target compounds that had been reported used in Granger Drain basin, 20 were detected. The two exceptions, terbufos and fonofos, likely were not detected because they were used in small amounts. The four most commonly detected compounds (two insecticides, carbaryl and trans-permethrin, one fungicide, myclobutanil and one herbicide, dacthal)) were detected in all or all but one of the samples. Pesticide transformation products are not often targeted in environmental air samples, but this study targeted/analyzed for 11 of them. Chlorpyrifos-oxon (from chlorpyrifos) and 1-napthol (from carbaryl) were the two that were most frequently detected. Some fraction of the 1-napthol that was detected in the air could have been produced in the injector port of the gas chromatograph during analysis.

There were essentially no relations between detection frequency and use rank (r^2=0.18), mass used (r^2=0.10), mean concentration (r^2=0.16), and maximum concentration (r^2=0.10). Likewise, there were essentially no relations between maximum concentration and use rank (r^2=0.13) or mass used (r^2=0.31) or between mean concentration and use rank (r^2=0.16). The relation between mean concentration and mass used has a high correlation coefficient (r^2=0.93), but this relation is largely driven by two data points. This relation disappears when the logarithm of mean concentration is regressed against the logarithm of mass used (r^2=0.14). There is a weak relation between the logarithm of detection frequency and the logarithm of mean concentration (r^2=0.46) with a trend of increasing mean concentration with increasing detection frequency. There are a number of possible reasons for the observed lack of relations among use, detection frequency, and concentration, such as the environmental conditions that varied throughout the growing season, variable application timing and techniques, and the wide variability in the vapor pressures of the applied pesticides, which affects their degrees of volatilization.

A number of pesticides, such as dacthal, dieldrin, prometon, and tebuthiuron, were frequently detected in the air over Granger Drain basin, but had no reported agricultural use in the watershed during 2003. Dacthal is a herbicide commonly used on vegetables and applied with a conventional ground-rig sprayer at planting time in Washington. Although there is no reported use in Granger Drain basin, there is use outside of the basin in Yakima County and surrounding areas (United States Geological Survey, 2005). The presence of dacthal in the air suggests that it is either transported into the basin from other areas, that the use in the basin is under estimated, or both. The presence of dieldrin is a legacy from the 1960s. It is still frequently detected in surface waters and aquatic biota in this area (Munn and Gruber, 1997). Prometon is widely used for non-agricultural purposes (to control weeds long fence lines and rights-of-way), but has no agricultural use in Washington. It has been widely detected in a variety of environmental matrices in agricultural areas (Capel et al., 1999). Tebuthiuron also is used on rights-of-way in Washington (State of

Washington, 2005), but is not listed as having any agricultural use (United States Geological Survey, 2005).

Table 1. Use, detection frequency, and total concentration of the target chemicals in air in the Granger Drain basin, May – September 2003 and May 2004.

Compound (Purpose)[a]	Target Crop[b]	Mass Used (Mg)[c]	Use Rank[c]	Detection Frequency (%)[d]	Air Concentration	
					Mean ± SD (ng/m^3)[d]	Maximum (ng/m^3)
Target chemicals that were detected in greater than 50% of the samples						
Carbaryl (I)	A,G,O	21	3	100	22±60	280
Trans-permethrin (I)	A,C	0.70	14	100	1.7±1.3	4.3
Dacthal (H)	N	0	N/A[e]	95	0.27±0.51	2.3
Myclobutanil (F)	G,H,O	2.6	7	95	6.6±17	80
Cis-permethrin (I)	A,C	0.70	14	90	0.15±0.18	0.75
Chlorpyrifos-oxon (T)	---	---	---[f]	86	4.9±5.3	21
Metalaxyl (F)	H,O	0.057	23	76	0.85±.072	2.5
Acetochlor (H)	C	1.1	11	62	0.55±1.0	4.5
Trifluralin (H)	A,B,G,H,M	0.14	20	62	0.14±0.22	0.86
Malathion (I)	A,H,O,P	11	4	57	0.71±0.96	3.0
Alachlor (H)	B,C	2.6	6	52	0.33±0.62	2.64
Target chemicals that were detected, but in less than 50% of the samples						
Atrazine (H), Chlorpyrifos (I), Deethylatrizine (T), Diazinon (I), Diazinon-oxon (T), Dicrotophos (I), Dieldrin (I), Dimethoate (I), Ethion (I), Fenamiphos (N), Fenamiphos sulfone (T), Fipronil (I) , Hexazinone (H), Isofenphos (I), Iprodione (F), Malathion-oxon (T), Methidathion (I), Methyl parathion (I), Methyl parathion-oxon (T), Metolachlor (H), Metribuzin (H), Pendimethalin (H), Phorate (I), Prometon (H), Prometryn (H), Simazine (H), Tebuthiuron (H), 1-Naphthol (T), 4-Chloro-2-methylphenol (T), 2,6-Diethylaniline (T)						
Target chemicals that were not detected in any of the samples						
Benfluralin (H), Dichlorvos (I), Fonofos (I), Pronamide (H), Phorate-oxon (T), Terbufos (I), Terbuthylazine (H), 2-Ethyl-6-methylaniline (T), 3,4-Dichloroaniline (T)						

[a]: F= fungicide, H = herbicide, I =insecticide, N = nematocide, T = transformation product.

[b]: A = alfalfa, B = beans and peas, C = corn, G = grapes, H = hops, M = mint, O = orchard, N = not reported, P = Pasture and Grass.

[c]: From Payne et al. (2006). Not all pesticides that were used in Granger Drain basin were included as targets in this study, so there are missing numbers in the use rank list.

[d]: Calculated based on 21 samples. Air concentrations less than the detection limit were assumed to be equal to zero for the mean concentration calculation.

[e]:N/A = Not applicable, since there is no reported use in Granger Drain basin in 2003.

[f]: --- = Not applicable, use rank is related to parent pesticide.

[g]:N/L = This compound is not listed in the databases used by Payne et al. (2006).

Concentrations of the pesticides detected in the air in this study generally are in the same range that have been observed for these same compounds in other agricultural environments (Peck and Hornbuckle, 2005; Kuang, et al., 2003; Majewski et al., 1998; Foreman et al., 2000; Majewski and Capel, 1995) with mean concentrations in the range of 0.01 to 20 ng/m^3. In a few samples, concentrations of carbaryl and myclobutanil were substantially higher with maximum concentrations of 280 and 80 ng/m^3, respectively. There has not been any previously reported concentration of these pesticides in air in Washington.

The temporal air concentrations of carbaryl and its transformation product, 1-napthol, are shown in Figure 1. Most of the time, carbaryl was detected at small concentrations, but during periods of application, the concentration substantially increased. Carbaryl, used mostly in orchards throughout the spring and summer, is applied through a variety of methods including by sprinklers or aerially. Generally, 1-naphthol was detected only when the air concentration of carbaryl was >6 ng/m^3. The other frequently detected pesticides had similar temporal concentration patterns with generally low concentrations most of the time and one or two weeks of elevated concentrations during their application periods. Periods of elevated concentration occurred in the early and late summer for carbaryl and permethrin, spring for chlorpyrifos and trifluralin, early summer for dacthal, myclobutanil, and acetochlor and late summer for metalaxyl.

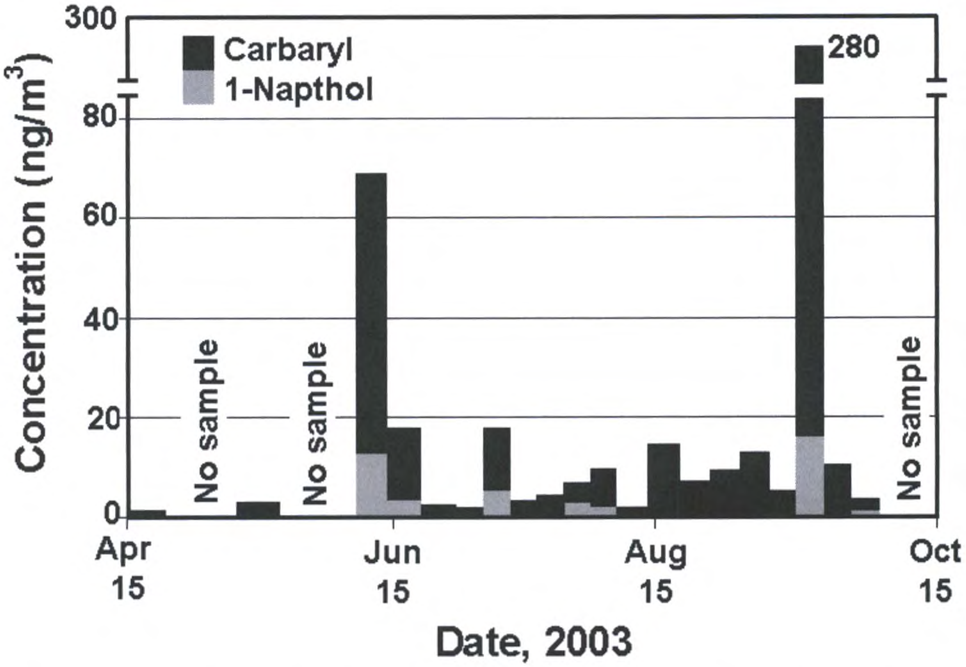

Figure 1. Concentration (vapor plus particulate) of carbaryl and 1-napthol in the air over Granger Drain basin during the 2003 growing season. Carbaryl was detected in every air sample during this period.

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Emissions Approaches and Uncertainties - Animal

Global Inventory of Ammonia Emissions from Global Livestock Production and Fertilizer Use

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Abstract

Ammonia is an important atmospheric pollutant with a wide variety of impacts ranging from aerosol formation, soil acidification, eutrophication, and biodiversity loss in ecosystems. One of the major global anthropogenic sources of atmospheric ammonia is animal waste generated in the production of meat, milk and other livestock products. We present a spatially explicit inventory of ammonia emission from global pastoral and mixed livestock production systems. Emissions are presented for grazing, animal houses and manure storage systems, and spreading of animal manure. We also discuss the major uncertainties in our inventory.

Introduction

At present the global use of synthetic fertilizer nitrogen (N) is about 80 billion kg yr^{-1}, and an even greater amount of animal manure N is generated in livestock production systems. The use of N fertilizer and the production of animal manure are expected to increase in the coming decades, particularly in developing countries (Bruinsma, 2003).

One of the major pathways of loss of N from agricultural systems is ammonia (NH_3) volatilization. This mechanism may be responsible for the loss of 10-30% of the N fertilizer applied or the N excreted by animals, and is the major anthropogenic source of atmospheric NH_3. Apart from NH_3, livestock production facilities, manure storage areas, and manure field-application sites are sources of particulate matter (PM10, PM2.5), volatile organic compounds (associated with odor or precursors for ozone formation), hydrogen sulfide, greenhouse gases (methane, nitrous oxides), and pathogens. In this paper we concentrate on emissions of NH_3 from global livestock production systems.

Any gaseous NH_3 present in manure, soil, water or fertilizer can volatilize to the atmosphere. Ammonia volatilization is driven by the difference in NH_3 partial pressure between the air and manure, soil, crops or floodwater, which is determined by many interacting factors (Bouwman et al., 2002a). Ammonia is an important atmospheric pollutant with a wide variety of impacts. In the atmosphere NH_3 neutralizes a great portion of the acids produced by oxides of sulfur and nitrogen. An important part of atmospheric aerosols, acting as cloud condensation nuclei, consist of sulfate and nitrate neutralized to various extents by NH_3. Essentially all emitted NH_3 is returned to the surface by deposition, which is known to be one of the causes of soil acidification (Van Breemen et al., 1982), eutrophication of natural ecosystems and loss of biodiversity (Bouwman et al., 2002b; Dise and Stevens, 2005).

In this paper we present a global inventory of emissions of NH_3 associated with livestock production and fertilizer use. This inventory is an update of the global emission inventory prepared in the framework of the Global Emission Inventory Activity (GEIA) project of IGBP-IGAC (Bouwman et al., 1997) and is a continuation of the work presented by Bouwman et al. (2005a,b,c). In this extended abstract we present global results, and briefly discuss uncertainties and research needs.

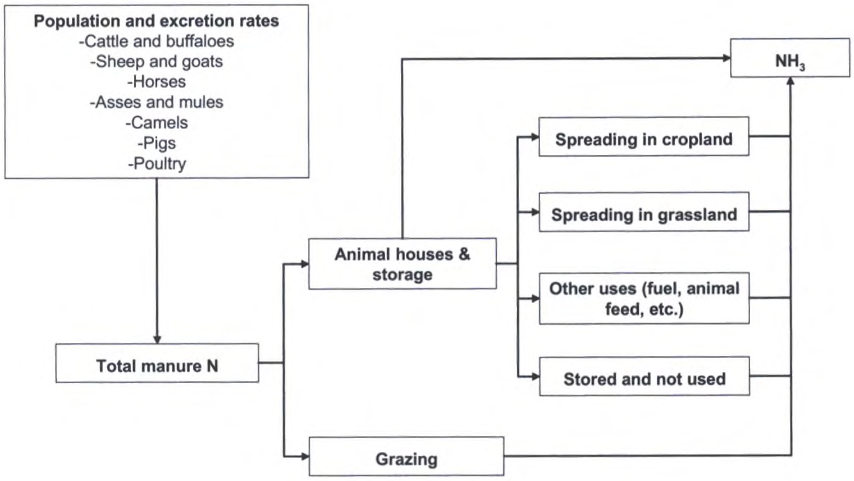

Figure 1. Distribution of manure over different management systems. This is done for both pastoral and mixed/industrial systems.

Data and Methods

We update the GEIA 1 by 1 degree resolution (~110 by 110 km at the equator) NH_3 emission inventory for the year 1990 (Bouwman et al., 1997) with data for the year 2000. In addition, the inventory is improved by using more detailed spatial information, by distinguishing different production systems and improved emission calculations for spreading of manure.

The global land cover map used in this study is based on a combination of two datasets from different satellite sensors, i.e. the IGBP-DisCover and the GLC2000 dataset (Klein Goldewijk et al., 2006). This land cover map includes cropland and grassland areas that are consistent with statistical information from FAO at the country scale and for some large countries at the state (U.S.A.) or provincial (China, Western Europe) level. The resolution is 5 by 5 minutes, which is about 8 by 8 km at the equator.

Within the areas of cropland and grassland we distinguish pastoral and mixed/industrial livestock production systems. In the pastoral production systems grazing is dominant and not integrated with cropping systems. Mixed/industrial systems have integrated cropping and livestock production, in which livestock production relies on a mix of food crops, crop by-products and roughage, consisting of grass, fodder crops, crop residues, and other sources of feedstuffs. In mixed systems the by-products of one activity (crop by-products, crop residues, and manure) often serve as inputs for another. We assume that the production system within a grid cell is mixed/industrial when cropland covers more than 15%. Otherwise the grid cell is considered to be dominated by pastoral production systems. This approach is similar to those of Kruska et al. (2003) and Bouwman et al. (2005c) and it yields a rough distinction between pastoral and mixed/industrial systems, although there may be large variation between countries.

With this land cover distribution as a basis, livestock manure is distributed over different systems (Figure 1). Ten animal categories are distinguished, including nondairy cattle, dairy cattle, buffaloes, pigs, poultry, sheep, goats, asses and mules, horses, and camels. We use data from FAO (2005) for animal populations and from national statistics for the states of the U.S.A., provinces of China and some regions in Western Europe. Associated N excretion rates are taken from Van der Hoek (1998). Excretion rates are assumed to be the same in mixed/industrial and pastoral systems.

First the livestock production for each animal category is divided into that in mixed/industrial and pastoral systems on the basis of data for world regions from Seré and Steinfeld (1996) and Bouwman et al. (2005c). On the basis of a-priori fractions for world regions manure is distributed within each country (or state or province) over grazing, animal housing and storage systems, other uses and stored but unused manure (Figure 1). The fraction grazing is derived from the ratio of grass to total feed in the ration of each animal category presented by Bouwman et al. (2005c). The fraction other uses and stored but unused manure is based on data presented by Mosier et al. (1998). In industrialized countries we assume that half of the stored manure is applied to cropland and the other half to grassland. In developing countries 95% is applied to cropland. In a number of countries the a-priori estimates for the manure distribution lead to unrealistic annual input rates. In such cases, the manure is re-distributed until annual N input rates are less or close to pre-defined maximum rates, which are 250 kg ha^{-1} yr^{-1} in mixed/industrial systems and 125 kg ha^{-1} yr^{-1} in pastoral systems.

Data on total N fertilizer use are from FAO (2005), fertilizer N use by fertilizer type from IFA (2003), and fertilizer use by crop from IFA/IFDC/FAO (2003). The difference between total use and application to grassland is assumed to be applied to cropland and evenly spread over the area of total cropland from Klein Goldewijk et al. (2006).

Ammonia volatilization rates for animal housing and grazing systems are taken from Bouwman et al. (1997). Volatilization from spreading of animal manure and fertilizer is calculated with the empirical model presented by Bouwman et al. (2002a) based on crop type, manure or fertilizer application mode, soil CEC, soil pH, and climate. Fertilizer type is used as a model factor for calculating NH_3 volatilization from fertilizers. All manure applied to cropland is assumed to be incorporated, while manure is applied to grassland by broadcasting. In the model incorporation leads to considerable reductions of NH_3 loss of up to 50% compared to broadcasting. We tentatively use an emission factor of 20% for the categories other uses and stored but unused manure.

Results and Discussion

The global N excretion by the ten animal categories amounts to 112 Tg yr^{-1}, of which 73% is generated in mixed/industrial systems, and 18% in pastoral systems (Table 1). The distribution over mixed/industrial and pastoral systems and the use of detailed spatial information allows for portraying the spatial variation of manure N inputs (Figure 2).

Within the mixed/industrial systems more than half of the manure N is collected in animal houses and storage systems, and 40% is excreted in pastures. For the pastoral systems 97% is excreted in pastures. According to our results about 10% of the global quantity of animal manure ends outside the agricultural system. This includes animal manure used as fuel, building material, animal feed or for other purposes.

The global NH_3-N emission from animal manure is about 24 Tg yr^{-1} (Table 1). More than 40% of this amount is from animal housing and storage systems, 30% is from grazing animals, and about 30% from spreading of animal manure. Emission of NH_3 from from N fertilizer use is about 11 Tg yr^{-1}

We compared our results with the emission inventory presented by Bouwman et al. (1997). For this comparison we applied the updated N excretion rates used in this study. Our new estimate of NH_3-N emission from global livestock production for the year 2000 (24 Tg yr^{-1}) is similar to the one based on the old methodology.

The sensitivity of our calculations to variation in parameter values was investigated for cattle, i.e. nondairy and dairy cattle. Total N excretion by cattle is about 64 Tg yr^{-1} which is about 57% of total N excretion by all animal categories in our analysis. Hence, variation of parameters related to cattle are expected to have an important influence of calculated NH_3 emissions. We selected the parameters N excretion per head, total N excretion in meadows relative to animal houses, and the NH_3 emission factors for animal housing (Table 2).

The results of this analysis indicate that N excretion per head has the largest influence (±15%) on global NH_3 emissions from livestock (Table 2). Varying total manure N generation in meadows relative to animal houses has less influence on global NH_3 emissions from livestock, because the importance of confinement of cattle in animal houses is much less important than for other animals such as pigs and poultry. Variation of the NH_3 emission factor for animal housing requires some explanation. With a higher NH_3 emission factor, less N is retained in the manure stored in animal houses and other storage facilities, and less is available for spreading. Since NH_3 loss rates from animal houses and other storage systems in our inventory are higher than for spreading, the overall emission rates also increase. In contrast, with a lower NH_3 emission rate more N is retained and more is available for application to cropland and grassland. The overall NH_3 emission thus decreases when the emission factor for animal houses is reduced.

Table 1. Global estimates of manure-N and NH_3 emission for animal housing and storage systems and grazing for mixed/industrial and pastoral systems, spreading of stored manure in cropland and grassland, and N fertilizer use for the year 2000.

Animal manure management system/ fertilizer use	Manure N production/use		NH_3-N emission	
	Gg yr^{-1}	% of total manureN	Gg yr^{-1}	Mean emission factor (%)
Mixed/industrial systems				
Storage	48677	43	9735	20
Grazing	33091	29	3474	10
Total	81767	73	13210	16
Pastoral systems				
Storage	581	1	116	20
Grazing	19327	17	2379	12
Total	19908	18	2495	13
Other uses	10757	10	2151	20
Spreading of stored manure[1]				
Cropland	33517	30	4835	14
Grassland	5889	5	1311	22
Total	39406	35	6145	16
Total animal manure	112432		24001	21
Total N fertilizer use	83024		10826	13

[1] Excluding 9852 Gg yr^{-1} NH_3-N loss from the total of 49258 Gg yr^{-1} in animal housing and storage systems.

Table 2. Effect[1] of variation of three important parameters for cattle on global NH_3 emission from livestock production.

Parameter	Variation -25%	Variation +25%
N excretion per head	86	115
N excretion in meadow[2]	104	96
NH_3 emission rate for animal housing	95	111

[1] The effect is expressed as an index value, with standard case = 100.

[2] Variation of N excretion in meadows also influences the N excretion in animal houses. More grazing gives less manure production by confined animals, and less grazing causes the manure collected in animal houses to increase.

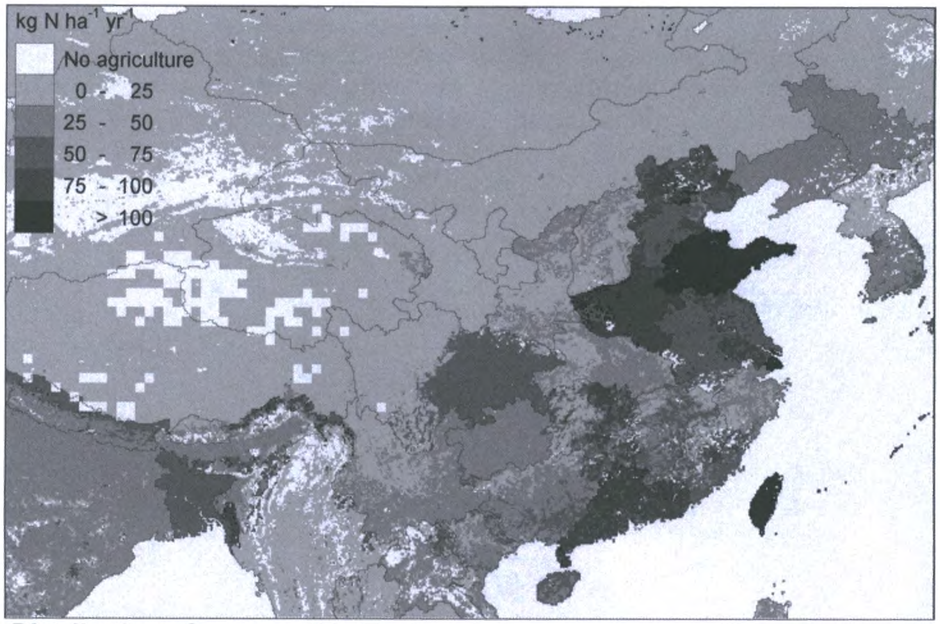

Figure 2. Distribution of manure N in Eastern Asia.

Concluding Remarks

In this paper we present an update of the GEIA global inventory of NH_3 emissions. Our inventory is largely based on country data (except for Western Europe, USA and China where more detailed information was included) on animal populations, areas of cropland and grassland, and information available for world regions on production systems (pastoral versus mixed/industrial), and the relative importance of grazing versus confinement of animals. New information can thus be used to modify any aspect of the inventory at the scale of countries or finer.

We recognize that there are several parts where further research and data collection is needed. We discuss four major issues. Firstly, the distribution of animal manure from ruminants over animal housing and other storage facilities and grazing may not be very important at the global scale, but locally it may have a very important influence on total emissions. In our inventory NH_3 loss from grazing systems is 10-12%, while that from animal housing and storage systems and spreading is much higher. The emission factor from animal housing and storage systems is rather uncertain. There are many different types of animal housing and storage systems worldwide, and NH_3 loss probably varies widely among them.

Secondly, in this inventory N excretion rates by animal category are average values for world regions, without a distinction between pastoral and mixed/industrial systems. N excretion rates may vary as a result of the productivity of the animal and the energy requirements. Meat and milk production per animal (higher in mixed/industrial systems than in pastoral ones) and the energy required for grazing and labor (lower in mixed/industrial systems) may result in N excretion rates that are not much different between the broad production systems. However, further research is needed to verify this assumption.

Thirdly, the distribution of animals over pastoral and mixed/industrial systems is derived from information for different levels ranging from world regions to countries or finer. Also the distribution of the grassland area in pastoral and mixed systems is based on the assumption that cropland covers at least 15% of the area in mixed agricultural systems. Although similar approaches have been used earlier for the developing countries, it is not clear if this method leads to realistic patterns in all parts of the world.

Fourthly, there is increasing concern about emissions of particulate matter (PM). An important research question is therefore if the data presented in this paper could be a starting point for an inventory of PM emissions.

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Hydrogen Sulfide Emissions from Southern Great Plains Beef Feedlots: A Review

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Abstract

Hydrogen Sulfide (H_2S) is emitted from animal feeding operations as a product of anaerobic breakdown of organic materials. There has been limited research efforts towards quantifying the H_2S emissions from open lot feedyards in the high plains of Texas, New Mexico, Oklahoma, Kansas and Colorado where more than 40% of U.S. beef cattle are fed and finished. As aerobic conditions are primarily observed in the feedyard manure packs, the ambient and property-line H_2S concentrations recorded are not as high as those associated with those intensive animal feeding operations where anaerobic conditions are primarily employed in treatment and storage systems. Exposure to high levels of H_2S can be fatal, while elevated levels can contribute to human health effects. Most states have regulations that set limits for ambient and/or property-line H_2S concentrations to protect public health. The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Emergency Planning & Community Right to Know Act (EPCRA) set reporting requirements for industries which exceed 100 lbs/day of long list of compounds including H_2S.

There have been a number of studies looking at ambient H_2S concentrations near open-lot beef cattle feedyards, Nebraska (Koelsch et al., 2004) and Texas (Rhoades et al., 2003; Koziel et al., 2004; See et al., 2003). Koelsch et al. (2004) monitored H_2S as total reduced sulfur (TRS) concentrations at three open-lot beef cattle feedyards in Nebraska reporting mean H_2S concentrations downwind of pens ranging from 0.006 to 0.013 ppm, with 19 of 2,067 total observations greater than 0.100 ppm. Mean concentrations downwind of ponds were 0.002 to 0.014 ppm, with 11 out of 1,888 total observations greater than 0.10 ppm and two greater than 10 ppm. Koelsch et al. (2004) concluded that "TRS levels in the vicinity of beef cattle feedlots are not likely to exceed current regulatory thresholds used by midwestern states". Rhoades et al. (2003) measured H_2S (TRS) concentrations upwind and immediately downwind of pens and ponds at three feedyards over a 12-month period in 2002-2003. The authors used a Jerome meter to measure short duration (i.e. over a two-minute interval) concentrations. Three to four readings were made at each location and averaged, thus each mean reading would be representative of about a 10 minute time span. The H_2S readings were taken during the day, usually between 9 AM and 3 PM. Koelsch et al. (2004) showed a diurnal pattern in H_2S emissions with higher emissions in the later afternoon when the temperatures were warmer. See (2003) also reported higher H_2S concentrations between 2 PM and 4 PM. Because all of Rhoades et al. (2003) data was taken in the daytime, it is unknown if this data if representative of true 24-hr emissions. The measurements of TRS made by Rhoades et al. (2003) showed average concentrations of 0.026 ppm at the feedyard pen fence and 0.037 ppm immediately downwind of feedyard retention ponds. See (2003) reported H_2S concentrations downwind of pens and pond for data collected during summer from a beef cattle feedyard in the Texas Panhandle. Hydrogen sulfide concentrations were measured using a Jerome meter and datalogger every 15 minutes for 44 hours downwind of pens and 22 hours downwind of the pond. See reported mean downwind H_2S concentrations of 0.005 and 0.005 ppm for the pens and ponds, respectively. Koziel et al. (2004) measured ambient H_2S concentrations at an open-lot beef cattle feedyard over three seasons (fall, winter, and spring) using a TEI 45C pulsed fluorescence analyzer housed in a instrument trailer. The trailer was located on the western side of the feedyard, immediately adjacent to the pens. Because the trailer was stationary, the wind direction variable, and its location upwind of the feedlot for one of the dominant wind directions, the instrument was not always recording downwind concentrations, the mean values presented in their research are likely skewed on the low side and not representative of true downwind mean concentrations. Mean H_2S concentrations for fall, winter, and spring seasons were 0.008, 0.001, and 0.002 ppm, while maximum H_2S concentrations were 0.030, 0.003, and

0.035 ppm, respectively. Koziel et al. (2004) concluded that "measured H_2S concentrations were always lower than the ambient air ground level concentration maximums for the State of Texas."

There is very limited data available on H_2S emissions from open-lot beef cattle feedyard pens with the only reported emission rates from open-lot beef cattle feedyards being collected as part of the Federal Air Quality Initiative project. Wood et al. (2001) reported a mean TRS emission rate of 103 μg/m^2/min from naturally ventilated, loose housed, beef steer housing facilities in Minnesota. Duyson et al. (2003) attempted to measure H_2S emissions using a wind tunnel and Jerome meter, however the concentrations were too low to quantify. Baek et al. (2003a,b) and Koziel et al. (2005) measured H_2S emission rates using a flux chamber (NC State design) and TEI 45C pulsed fluorescence analyzer. The data of Baek et al. (2003a,b) and Koziel et al. (2005) are summarized in Table 1. Based on these H_2S emission rate estimates, this equates to an extrapolated emission rate of 0.065-0.088 lb/d (0.029-0.040 kg/d) per 1,000 head using a stocking rate of 14.7 m^2/head. For a typical 50,000 head feedyard, this equates to an emission rate of 3.2-4.4 lb/day from the pens only.

Table 1. Hydrogen sulfide emission rates from two beef cattle feedyards measured using a flux chamber

Reference	CAFO Type	Method	Emission Rate (μg/m^2/min)
Baek et al. 2003a,b	Beef Open-Lot	Flux Chamber	1.88
Koziel et al. 2005	Beef Open-Lot	Flux Chamber	1.39

No published estimates of H_2S emission rate from the runoff retention structures at open lot beef feedyards have been found in the published literature. Conditions in these runoff retention structures are usually slightly acidic and anaerobic with accumulating, decomposing organic matter. These conditions are conducive to H_2S generation and emission. While the area of the runoff retention structures is less than the pen area in a typical feedyard, it could be safely assumed that the emission rate is greater on a per area basis and these emissions may dominate the overall emissions from the facility.

Conclusions

Based on the measurements of downwind H_2S concentrations available from the published literature, it appears that there is a low probability that the average H_2S concentration downwind of a feedyard will exceed the ambient downwind H_2S regulatory values for Texas of 80 ppb (30 minute average), however that it is possible during critical atmospheric conditions. Assessment of the potential of a feedyard to exceed the CERCLA/EPCRA reporting requirement of 100 lbs/day is not currently possible given the lack of any published data regarding emissions from the potentially significant runoff retention structures. Measurements of the emission rate from these runoff retention structures is urgently needed to complete this assessment.

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Emission of Nitrous Oxide from NE Dairy Farms and Agricultural Fields: Laboratory and Field Studies

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Abstract

Agriculture significantly contributes to overall anthropogenic N_2O emissions. The input from stored animal waste can be as great as 3% of total agricultural emission. Dairy farms are ubiquitous in New York State and their contribution to nitrous oxide emissions is unknown. The goal of this study is to quantify N_2O losses from large dairy farms and agricultural fields as influenced by interactions between tillage practices, soil conditions and manure application. We summarize here both laboratory and a portion of field experiments. At the conference we will report N2O emissions measured using Tunable Diode Laser Trace Gas Analyzer (TDL TGA). We will discuss nitrous oxide emission rates from the various agricultural fields and recommend improvements in manure management schemes to reduce greenhouse losses.

Introduction

Global agricultural N inputs to the atmosphere now exceed those from natural sources. One of the main sources of gaseous N losses is spreading of animal waste on agricultural fields, amounting to 35% of the global annual emission (Kroeze et al., 1999). The Kyoto protocol commits signatories to reducing greenhouse gas emissions to 1990 levels.

A number of experimental studies have measured nitrous oxide emissions from agricultural fields (e.g. Gregorich et al., 2005). The results were interesting but also indicate large uncertainties and variability in both time and space arising from soil heterogeneity and complex interactions between chemical, physical and biological variables (e.g Muller et al., 1997). More research is needed to obtain a quantitative understanding of how farm management practices can reduce N_2O emissions. Of special interest is learning and solving some of the apparent complexities involving the interactions between tillage practices and soil conditions and how the affect N_2O emissions shortly after manure application when potential losses are the greatest. A good example of the complexities involved in designing manure management strategies is the practice of manure injection into soil to reduce odor emissions following spreading of both liquid slurries and farmyard manures (Webb et al., 2004). Although this is known to reduce ammonia emissions, there are concerns that these direct applications into soil may significantly increase N_2O emissions by increasing the pool of mineral N in soil (Bouwman, 1996).

To improve our understanding on the interactions between tillage effects, moisture content, manure application and chemical, physical and biological variables we are carrying out laboratory and field experiments. We will summarize here on the laboratory and some of the field experiments. At the conference itself we will report on current determinations of nitrous oxide emissions measured using Tunable Diode Laser Trace Gas Analyzer (TDLTGA), which have been delayed due to technical breakdowns.

Experimental

Laboratory Experiments

Materials: Two sand textures – coarse and fine – were used consisting of washed organic- free sand with particle diameters of 1 and 0.25 mm, respectively. Total porosity was ~36% in both cases. The synthetic urine mixture contained urea-N concentrations to simulate levels of dietary N intake (11.5 g/L), as well as glycine (2.9 g/L), $KHCO_3$ (13.8 g/L), KCl (2.5 g/L), KBr (4.2 g/L), and K_2SO_4 (1.4 g/L), with 0.5% of cow urine added. The experimental chambers were sealed plastic desiccators (14-cm diameter, Bel-Art No.F42010) packed with 1 cm or 5 cm sand depths. All experiments were repeated in triplicates and carried at constant temperature of 25°C.

Incubation procedure:

(1) Static headspace experiments: synthetic urine was added to each sand to bring the sand moisture content to 10, 15, 30, 50, 60, 70, 85, and 90%. The wetted sand samples were sealed in the chambers and incubated in aerobic conditions at the constant temperature. Samples of headspace air (6 mL) were taken twice a day. After each sampling, the sample units were opened to room atmosphere and then sealed again. Every second day the chambers were weighed to monitor the moisture loss by evaporation. The total duration of each treatment was 30 days.

(2) Flow-through experiments. Nitrous oxide-forming processes were linked to the changes of urine distribution with depth caused by evaporation. Both sand textures were mixed with urine to reach 80% water-filled pore space. The experiments were carried out with constant air flow rates using an air pump. Air was injected at the flow rate of 1250 mL/min during the first 24 hours and thereafter reduced to 125 mL/min; air samples were taken from tubing near input and output ports with syringes every 4 hours during the first two days and then every 8 hours during 14 days. The air samples were analyzed for N_2O concentrations.

Field Experiments

Field site: The research site is located on a large dairy farm central New York (42°49'N, 76°47'W), 15 miles from city of Ithaca. The site is a cornfield, which receives dairy manure fertilization once a year, in spring or fall. Manure is injected into the field with a tractor and a draghose (Wright and Bossard, 2003). On 10 October 2004 all the equipment for flux measurements and soil sampling was installed in the field (after corn harvesting and about 6 months after the last fertilization). The experiment was continued till December 5, 2005. On November 7 one half of the field was tilled.

Measurements of nitrous oxide flux using chambers: Accumulation of nitrous oxide was determined using polyvinylchloride chambers covering a rectangular area of 0.89 m^2. Each chamber consisted of a frame permanently located in the ground which could be sealed for 3 hours with removable plastic lid and additional plastic film isolation to prevent air exfiltration from the chambers. Each chamber lid was equipped with an aperture tightly closed by rubber septa to allow gas sampling with a syringe. Gas samples were collected at the start and termination of sealing in evacuated minivials. The nitrous oxide concentrations were measured by gas chromatography (GC) with an electron capture detector. The instrument used was Varian 3700 GC with a manual injection system and Ni^{63} ECD operated at 350°C. The carrier gas was $Ar:CH_4$ (95:5) at a flow rate of 30mL/min.

Soil sampling and analysis: Soil samples were collected from the depth of 15-20 cm near each chamber when the air samples were collected. Samples were transported for the laboratory where were analyzed for NO_3^-, NH_4^+, pH, and gravimetric moisture content (Franson,1985).

Results and Discussions: a Summary of our Findings

The Effect of the Soil Moisture-filled Pore Space (MFPS) and Temperature on N_2O Emission

Laboratory experiments with urine. Figure 1 demonstrates the mean N_2O flux during the laboratory static headspace experiment from sand surface as a function of urine-filled pore space. For both sand types N_2O emission was observed between 20 and 70 % of urine-filled pore space and reached maxima at ~50%. The general shape of the curves corresponds to the shape of relationship between N_2O emission and moisture-filled porosity presented by Davidson et al. (2000) for different soil types.

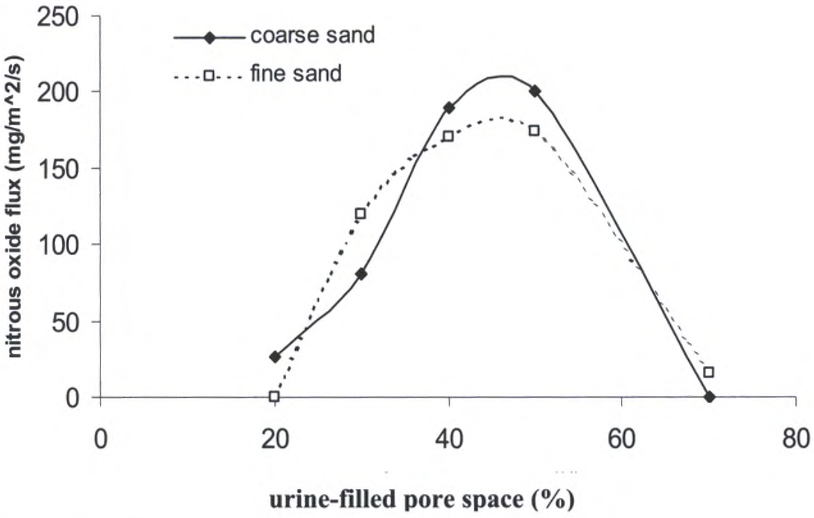

Figure 1. A generalized relationship between urine-filled pore space and N_2O flux in two sand types (controlled conditions)

Figu tion of N converted to N_2O) at the different sand depths. In general, the most gaseous emission of N_2O was found within the ~30-60% range of urine-filled pore space in both sand types, which corresponds very well to Figure 1. The thickness of the horizon containing ~30-60% urine-filled pore space was greater in the fine sand, therefore the production of N_2O was more intensive in this sand type. In fine sand (Figure 2a), the thickness of this zone with this porosity range increased from 1 cm to 3 cm from during days 4 to 8 of the experiment, and then decreased to 1 cm after 16 days. In contrast, in coarse sand (Figure 2b), the width of this horizon was a constant ~1 cm throughout the experiment. In both sands the N_2O production horizons moved deeper with time because of the sand drying process. A more detailed description can be found in Singurindy et al. (2006).

Field data. Nitrous oxide flux measured in the cornfield soils is presented in Figure 3 as a function of soil water-filled pore space and soil temperature. The nitrous oxide emissions are represented by the colored spectrum. The maximal flux of nitrous oxide was found when at the water-filled pore space ~ 55%, which corresponds well to the results obtained in the laboratory as presented in Figure 1. Generally, the optimal conditions for nitrous oxide production were found for the temperatures greater than 5°C and at water-filled porosities between 40 and 70 %. Temperatures lower than 5°C reduced microbial activity in the soil that reduced emissions.

(a) (b)

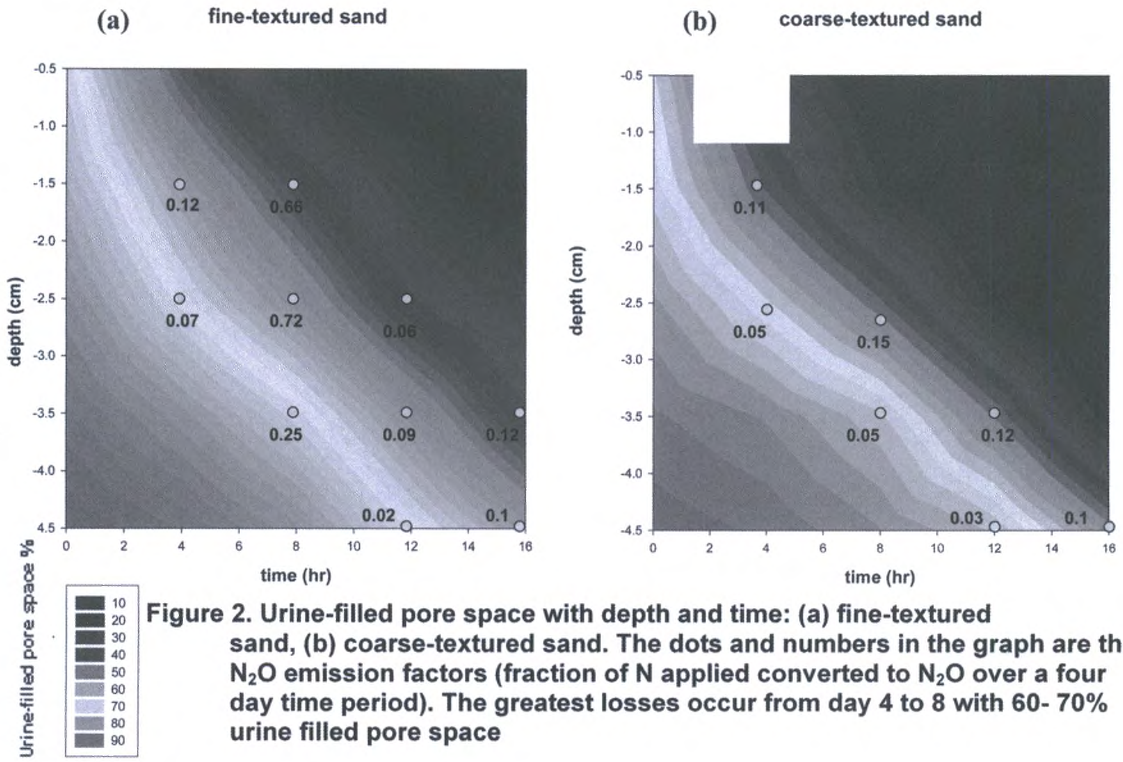

Figure 2. Urine-filled pore space with depth and time: (a) fine-textured sand, (b) coarse-textured sand. The dots and numbers in the graph are the N_2O emission factors (fraction of N applied converted to N_2O over a four day time period). The greatest losses occur from day 4 to 8 with 60- 70% urine filled pore space

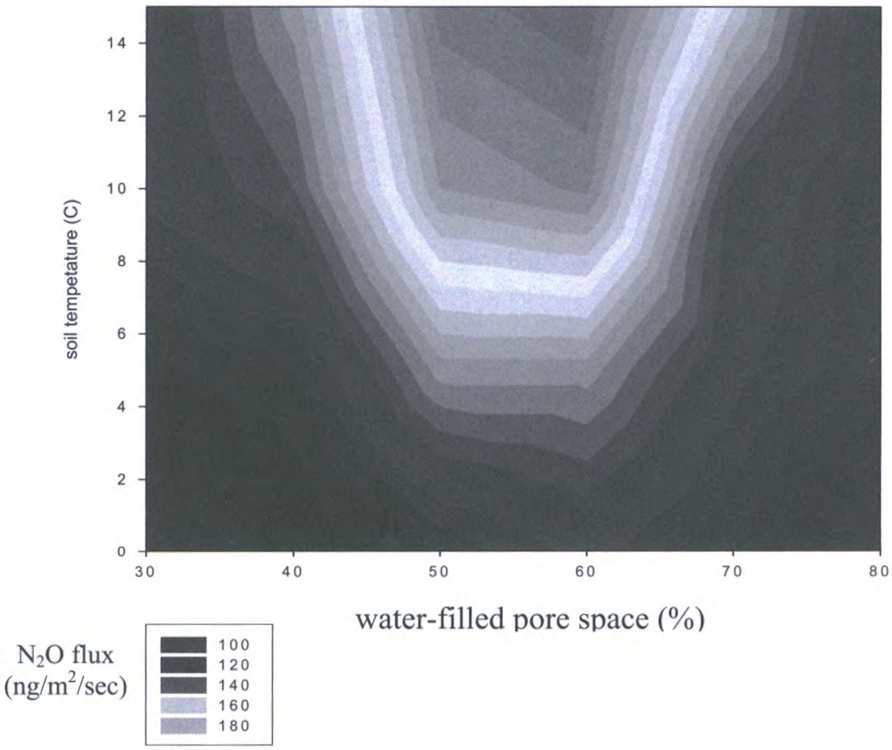

Figure 3. Generalized changes of nitrous oxide flux with temperature and water-filled pore space, field data.

Figure 4 presents the nitrous oxide flux from agricultural field. In non-tilled soils, the significant increase in the flux began one day after intensive precipitation (events 1 and 3), then the flux decreased by 2.5 times after ~70 mm of precipitation in both events. In contrast, the intensive precipitation caused increases in the flux in tilled soils during the whole precipitation event (event 3). Tillage resulted in immediate decrease for ~50% of nitrous oxide emission. These results suggested that denitrification was the dominant process in soils before tillage. Plowing improved aeration conditions in soil and reduced the soil WFPS which was reflected in short-term increase of nitrous oxide (event 2) two days after plowing. This peak corresponds to the increase on nitrate concentration in tilled soils (data are not presented).

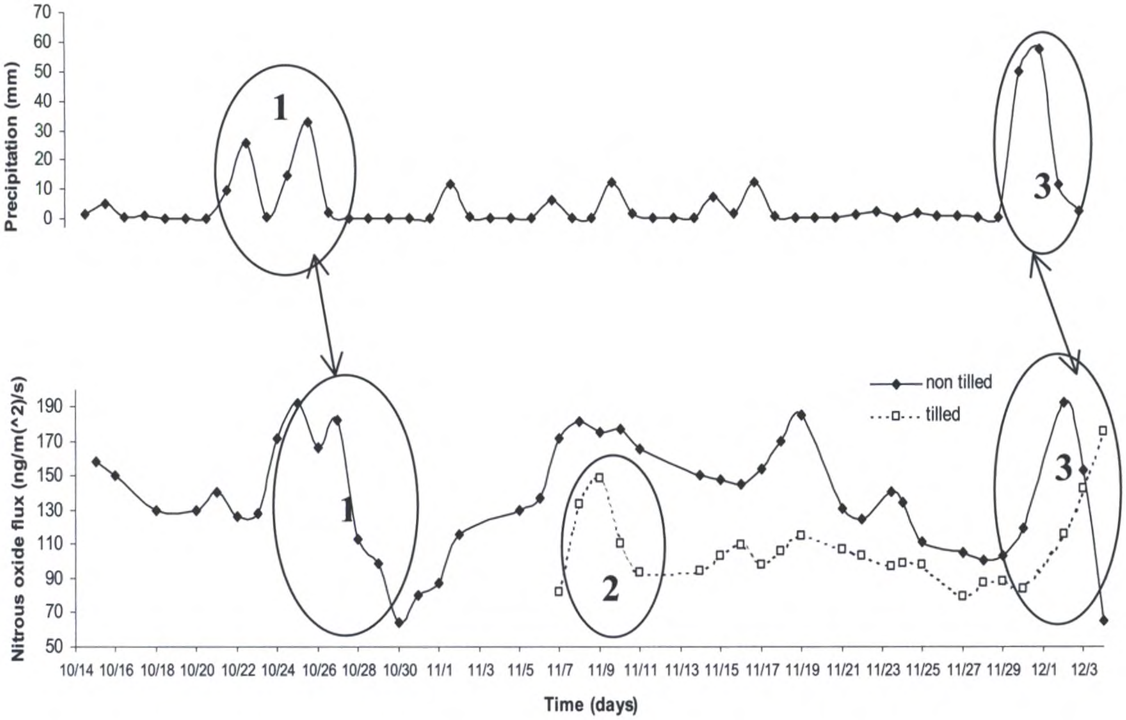

Figure 4. Fluxes of nitrous oxide measured from tilled and non-tilled parts of the agricultural field.

Conclusions

The presented results demonstrate that tillage has a significant effect on fluxes of nitrous oxide. Tillage increased nitrate concentration for short-term that was not observed in non-tilled soils The MFPS determined during each nitrous oxide sampling related to nitrous oxide fluxes indicated that the differences in the fluxes were mainly due to moisture content and temperature fluctuations in the field that controlled the intensity of microbial activity. Generally, tillage reduced nitrous oxide emission before manure application.

Since short-term pulses nitrous oxide occurring after tillage and wetting events are a significant component of annual nitrous oxide flux in the NE dairy farming and vary spatially and temporally it is necessary to determine nitrous oxide fluxes in agroecosystem using accurate measurements using Tunable Diode Laser Trace Gas Analyzer (TDLTGA). Further research is under way to examine the influence of other soil quality indicators and depths of manure injection on nitrous oxide emission from agricultural soils.

Acknowledgments

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Quantification of Gas, Odor and Dust Emissions from Swine Wean-Finish Facilities

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Abstract

A total of 1,920 pigs (equal barrows and gilts) are being used in a 2 x 2 factorial, wean to finish experiment to determine the effects of diet (control, CTL vs. low nutrient excretion, LNE) and manure pit management strategy (deep pit, DP vs. monthly pull plug, PP) on excretion of nutrients and gaseous and particulate emissions. Pigs are being housed in a 12 room environmental building, which allows for real-time monitoring of air quality, and quantitative manure collection from 24 pits (2/room). Each room contains 30 barrows (3 pens) and 30 gilts (3 pens), which are being split-sex and phase fed to meet or exceed the nutrient requirements of pigs (NRC, 1998) at different stages of growth. Dietary treatments (CTL and LNE) are being maintained throughout the trial. Individual pig weights and pen feed consumption data are collected every two weeks. Four pigs from each pen are being scanned ultrasonically for determination of loin eye area and backfat thickness at two months of age and every four weeks thereafter during the study. At the end of the experiment, carcass data is being collected at harvest on all pigs. Air temperature, relative humidity, total suspended particulates, ammonia, hydrogen sulfide, carbon dioxide, and methane concentrations are being recorded every fourth week during the experiment. In addition, odor samples are being collected at months 1, 3 and 5 of each wean-finish replicate in this experiment. A dynamic dilution venturi olfactometer is being used, with trained panelists, to evaluate each bag sample of air for olfactometry. Odor and gaseous emission rates are being calculated by multiplying air flow rate by the difference between inside and outside concentrations. Preliminary data indicates that pigs fed the LNE diet grow faster than control fed pigs while consuming less feed, resulting in an improved feed efficiency throughout most phases of the trial.

Introduction

In the past two decades, the pork industry has undergone rapid technological and structural change. The most significant changes have been a decrease in farm numbers, an increase in production facility size, and the movement of large production operations to more rural areas of the country. The number of farms raising hogs declined by 83% form 1965 to 1995 (USDA Report, 1996). Additionally, from 1997 to 2002, the number of farms with swine decreased by 45.7% or an average of over 9% per year (USDA report, 2002). Even though the swine industry has seen record losses of farms, relatively little change in the annual number of pigs raised in the US has occurred between 1965 and 2002. Unfortunately, animal feeding operations can affect air quality through emissions of odor, odorous gases (odorants), particulates (including biologic particulate matter), volatile organic compounds, and some greenhouse gases (Arogo et al., 2001; Bicudo, et al., 2001; Sweeten, et al., 2001; USDA AAQTF, 2001; and NAS, 2003). Much of the emitted gases come from the anaerobic decomposition of manure during storage, the release of volatile organic compounds and ammonia immediately after excretion from the animal and dust generated in the building facilities from feed delivery systems, animal movement, and hair and sloughed skin from the animal. New regulatory pressures to meet water and air quality standards for CAFO's (EPA, 2003) and NPDES permit regulations, including the possibility of meeting total maximum daily load (TMDL) of contaminants in the water supply and stricter air quality regulations are placing additional economic and management burdens on pork producers which may lead to further consolidation of the industry.

Much of the public awareness of the potential threat of swine manure to water pollution has been due to a few large operation's having spills. Media attention and activity groups have applied pressure on producers, legislators and regulators for management changes in livestock operations. In many cases, odors, dust and gas emissions from swine units have resulted in nuisance lawsuits and unrealistic regulations not necessarily based on scientific evidence. Residents near operations are concerned about the potential devaluation of their property and the impact of manure and odors on their health and lifestyle. State and local governments are struggling to develop long term land use plans to maintain sufficient land areas for both pork operations with land application of manure and the influx of urban residents into rural areas. Therefore the objectives of this trial are to determine the amount of gases, odors and dust emitted from buildings when swine are fed different diets and two manure storage strategies are utilized.

Materials and Methods

Animal Design

To date, 960 (avg initial BW = 5.16 kg; avg final BW = 128.16 kg) wean-finish pigs have been utilized. Pigs were housed in an environmentally controlled building with identical and independent ventilation, feeding systems, water, and manure storage pits. Each room housed 10 pigs per pen with 60 pigs per room. Pigs were blocked by BW and sex (10 pigs/pen; 60 pigs/room) and randomly allotted to 1 of 4 treatments arranged in a 2 X 2 factorial design with 2 diet formulations (standard commercial corn-SBM control, CTL; or a low nutrient excretion diet, LNE) and 2 manure storage strategies (6 month deep pit collection, DP; or a monthly pull plug/recharge collection, PP). Pigs were split-sex and phase fed to meet or exceed nutrient requirements (NRC, 1998). This trial consisted of five nursery phases and four grow-finish phases. The nursery phases included: 1) Pellets, d 0-7; 2) Phase 1, d 7-14; 3) Phase 2, d 14-28; 4) Phase 3, d 28-42; and 5) Phase 4, d 42-56. The grow-finish phases included: 1) Grower 1, d 56-84; 2) Grower 2, d 84-112; 3) Finisher 1, d 112-140; and 4) Finisher 2, d 140-152. Individual pig weights and pen feed consumption data were collected once a week during the nursery pellet phase and phase 1, then every two weeks thereafter. Four pigs from each pen were scanned ultrasonically for determination of loin eye area and 10th rib backfat thickness starting at two months of age and every four weeks thereafter during the study. At the end of the experiment, carcass data were collected at harvest on all pigs by a commercial slaughter facility.

Dietary Treatments

Pigs were fed either a commercial corn-soybean meal control (CTL) diet or a low nutrient excretion (LNE) diet (Table 1). The LNE diets had a reduced crude protein level compared to the CTL diets, and included synthetic amino acids, phytase (Natuphos, BASF, New Jersey, USA), added fat, and a non-sulfur trace mineral premix. Diets were formulated based on NRC (1998) requirements for available phosphorus and true ileal digestible amino acids, while also maintaining similar lysine:calorie ratios.

Air Concentration Monitoring

Continuous real-time instruments monitored ammonia (NH_3), hydrogen sulfide (H_2S), carbon dioxide (CO_2), and methane (CH_4) every fourth week during the trial. Real-time monitoring was conducted for 5 days during the fourth week before the release of manure from the pit in the PP system, during pit sampling and for 2 days after pit emptying to determine any effect of emptying a manure pit on gas emissions.

Thirty nine odor samples were collected at months 1, 3, and 5 of each replicate with three samples obtained from each room exhaust and three from the fresh air plenum that is common to all rooms. The three odor samples obtained from each room were collected at each measurement location simultaneously. Air samples were collected into 10 L Tedlar bags. A dynamic dilution venturi olfactometer (AC'SCENT Internations, St. Croix Sensory, Inc., St. Paul, MN) was used to evaluate each bag sample of air for olfactometry (data not presented). All evaluations were performed by trained human panelists. Sample evaluation occurred the same day as sampling to minimize bag losses.

Statistical Design

All data were analyzed using the GLM procedure of SAS (2006; SAS Institute Inc., Cary, NC). Pen was the experimental unit for animal performance and carcass characteristics; data represents 48 of 72 planned observations for diet and sex. Manure pit was the experimental unit for manure storage strategy and data presented represents 16 of 24 planned observations. Finally, room was the experimental unit for aerial gaseous compound concentrations; data represents 8 of 12 planned observations for diet and storage and 16 of 24 planned observations for wk of production. Animal performance and carcass characteristics were analyzed for the main effects of dietary treatment, manure storage type, and sex. Gaseous and particulate emissions were analyzed for the main effects of dietary treatment, manure storage type, and week of production.

Results

Nursery Performance

During nursery phase 1 (Table 2), CTL fed pigs had a 7.8% increase (2.96 vs. 2.73 kg/d; $P<0.02$) in average daily feed intake (ADFI) compared to LNE fed pigs, however diet did not affect average daily gain (ADG) or feed efficiency (Gain:Feed). During this phase gilts tended to have increased feed efficiency compared to barrows (0.72 vs. 0.67, respectively, $P<0.08$). In phase 2 of the nursery period there were no differences in ADG or ADFI, however numerical differences in these parameters resulted in an increased feed efficiency for LNE fed pigs compared to CTL fed pigs (0.77 vs. 0.73, respectively; $P<0.05$). Gilts tended to have increased ADFI compared to barrows ($P<0.07$). During phase 3, LNE fed pigs had a 6.3% increase ($P<0.001$) in feed efficiency and tended to have an increased ADG ($P<0.08$) compared to CTL fed pigs. During phase 4 (d 42 to 56) of production, growth performance of LNE fed pigs was superior to CTL fed pigs. The LNE diet increased ADG by 4.5% ($P<0.003$) and decreased ADFI by 8.6% ($P<0.002$) which resulted in a 12.9% increase ($P<0.001$) in feed efficiency. Although growth performance was improved with the LNE diet throughout the nursery phase, there was only a tendency for LNE fed pigs to be heavier on d 56 than CTL fed pigs (35.53 vs. 34.58 kg; $P<0.06$). However since this data remains preliminary, we expect as our sample size increases there will be a separation in BW between the two dietary treatments resulting in LNE fed pigs being heavier at the end of the nursery period.

Grow-finish Performance

Manure storage type did not have any effect on grower 1 growth performance (Table 3). However, ADFI was increased by 7.6% ($P<0.003$) and feed efficiency was decreased by 8.0% ($P<0.003$) for CTL fed pigs compared to LNE fed pigs. During grower 1, barrows had greater ADG than gilts ($P<0.006$), but d 84 BW was not different between sexes (61.38 vs. 60.39; $P=0.15$). Pigs fed the LNE diet during grower 2 had a 10.2% increase in ADG, a 14.6% increase in G:F, and a 4.5% decrease in ADFI ($P<0.02$) compared to CTL fed pigs. LNE fed pigs also weighed approximately 3.4 kg more than CTL pigs on d 112 (91.36 vs. 88.01 kg; $P<0.002$). These improvements in growth performance continued throughout the two finisher 2 phases. LNE fed pigs were 4.3 and 5.0 kg heavier at d 140 and at market (d 152) compared to CTL fed pigs ($P<0.001$). Additionally, barrows were heavier ($P<0.04$) following the end of grower 2, finisher 1, and finisher 2 compared to gilts. Manure storage type only had a significant affect on grower 2 ADFI, where pigs reared under the DP system consumed 4.3% more feed per day than pigs reared under the PP system.

Carcass Characteristics

Live ultrasonic measures of loin eye area and backfat thickness were unaffected by sex during the grower 1 and 2 phases (Table 4). However, LNE fed pigs had greater backfat thickness compared to CTL fed pigs during grower 1 and 2 (8.85 vs. 8.01 mm and 11.07 vs. 9.50 mm, respectively; $P<0.004$). Pigs fed LNE diets also showed a tendency for a greater loin eye area for grower 1 (14.52 vs. 13.82 cm^2; $P<0.08$). Dietary effects on backfat thickness were observed throughout the experiment. Backfat depths for LNE fed pigs were 9.5, 14.2, 10.4, 12.3, and 13.8% higher than CTL fed pigs for grower 1, grower 2, finisher 1, finisher 2, and market, respectively ($P<0.004$). These results are not surprising since LNE fed pigs were heavier than CTL fed pigs at the end of grower 2, finisher 1, and finisher 2 (Table 3). Backfat thickness was also 13.1, 20.9, and 19.5% greater in barrows for finisher 1, finisher 2, and market, respectively, compared to the gilts. Again this result can be explained by the fact that barrows were heavier than the gilts during the grower 2 and finisher phases.

Similar to live ultrasonic measures, carcass backfat thickness, lean percent, carcass grade premium, and hot carcass wt were all affected by dietary treatment (Table 5). Carcass backfat thickness was 8.6% greater ($P<0.000$) in LNE fed pigs, compared to CTL fed pigs. Pigs fed LNE diets also had a decreased lean percentage compared to CTL fed pigs (53.24 vs. 53.80%; $P<0.001$). Although the live ultrasonic measurements indicate a larger loin eye area for LNE fed pigs, carcass loin depth measurements were not different among dietary treatments. Decreased lean percentages and increased backfat resulted in a reduced carcass grade premium for LNE fed pigs compared to CTL fed pigs ($0.10 vs. $0.11 per kg; $P<0.003$).

However, hot carcass wt was increased by 3.7 kg (96.72 vs. 93.13 kg; $P<0.003$) for LNE fed pigs compared to CTL pigs. Therefore, overall carcass value was not different for LNE and CTL fed pigs.

Barrows had 16.3% more backfat ($P<0.001$) and a heavier hot carcass wt ($P<0.002$) compared to gilts, which were leaner than barrows (54.06 vs. 52.98%; $P<0.001$). Carcass grade premium, carcass value, and live value for gilts were increased ($P<0.05$) by 25, 2.9, and 2.9%, respectively compared to barrows.

Gas Concentrations

Data presented in this section is preliminary and consists of gaseous concentrations only. Air flow data is being calculated to determine gaseous emission rates. Gas concentration data collected from May 2005 to January 2006 reveals that diet, manure storage type, and week of production have significant effects on the concentration of various gaseous compounds (Table 6 and 7). Based on preliminary data, LNE diets reduced aerial NH_3 concentration over the wean-finish period by 13.6% ($P<0.001$) compared to CTL diets. The PP system significantly reduced aerial NH_3 concentrations by 7.3% ($P<0.005$) compared to the DP system. The PP system also reduced aerial CH_4 concentration by 17.7% (9.44 vs. 11.47 ppb; $P<0.001$) compared to the DP system. Aerial H_2S and SO_2 concentration were not different ($P>0.10$) among dietary treatments even though LNE diets were formulated with a non-sulfur trace mineral premix. Additionally there was no effect of manure management system on H_2S concentration (139.38 vs. 138.76, respectively; $P>0.10$). However, the PP system tended to increase aerial SO_2 concentration compared to the DP system (12.71 vs. 9.90 ppb, respectively; $P<0.07$).

Air concentration data was also affected by wk of production, except for aerial SO_2 concentration (Table 7). Aerial NH_3, H_2S, and CH_4 concentrations were increased by 43.4, 68.3, and 29.0%, respectively, from wk 4 to wk 16 ($P<0.001$). Conversely, the concentration of CO_2 was reduced by 13.6% during wk 20 compared to wk 4 ($P<0.001$).

Implications

The most significant change seen in the swine industry has occurred over the last sixty years. We have seen a shift from many farms producing a limited number of pigs to a small number of large confinement production facilities. New regulatory pressures to meet water and air quality standards for CAFO's and NPDES permit regulations are placing additional economic and management burdens on pork producers, which may lead to further consolidation of the swine industry. Preliminary data presented in this proceedings paper illustrates that feeding low nutrient excretion diets does not have to result in poor animal performance or carcass characteristics to yield reductions in gaseous compounds. Pigs fed the low nutrient excretion diets had improvements in average daily gain, feed efficiency, and were approximately 5.0 kg heavier at market than pigs fed control diets. Although backfat thickness was greater for low nutrient excretion fed pigs, there was no difference in percent carcass yield or total carcass value. More data needs to be analyzed to determine accurate air emission data from this trial, however by reducing emissions from swine facilities; there can be less neighborly concern and more acceptance of the swine industry. Moreover, this data will serve as a modeling tool for producers, extension educators, regulators, consultants, and legislators to plan environmentally sound pork production systems throughout the Unites States.

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Table 1. Dietary Treatments for Finisher 1.

	Control		LNE	
Ingredients, %	Barrows	Gilts	Barrows	Gilts
Corn	81.05	79.27	81.66	79.68
Soybean meal	17.00	18.79	12.03	14.01
Choice white grease	------	------	4.00	4.00
Calcium carbonate	0.66	*0.65*	*0.90*	*0.90*
Dicalcium phosphate	0.70	0.69	0.34	0.33
Vitamin premix	0.10	0.10	0.10	0.10
TM preminx	0.05	0.05	------	------
Non-sulfur TM premix	------	------	0.05	0.05
Phytase	------	------	0.083	0.083
Salt	0.25	0.25	0.25	0.25
Lysine-HCl	0.10	0.10	0.32	0.32
DL-methionine	------	------	0.05	0.06
L-threonine	0.01	0.02	0.12	0.12
L-tryptophan	------	------	0.02	0.02
Tylan 40	0.025	0.025	0.025	0.025
Se 600	0.05	0.05	0.05	0.05
Calculated Analysis				
ME, kcal/kg	3347	3346	3517	3517
Lysine:calorie ratio	2.101	2.235	2.101	2.235
Calcium, %	0.50	0.50	0.50	0.50
Avail. Phosphorus. %	0.19	0.19	0.19	0.19

Table 2. Effects of diet, manure storage type, and sex on nursery pig performance (preliminary data)[a].

	Diet		Storage		Sex			P Values		
Main Effects	Control	LNE	Deep Pit	Pull Plug	Barrows	Gilts	MSE	Diet	Storage	Sex
Initial wt, kg	5.15	5.17	5.15	5.16	5.22	5.10	0.800	0.94	0.95	0.46
d 7 wt, kg	6.11	6.12	6.11	6.11	6.16	6.06	0.758	0.98	0.99	0.50
Phase 1 (d 7 to d 14)										
ADG, kg/d	0.21	0.19	0.19	0.21	0.19	0.21	0.052	0.25	0.03	0.11
ADFI, kg/d	2.96	2.73	2.83	2.86	2.82	2.87	0.483	0.02	0.78	0.60
Gain:Feed	0.69	0.70	0.65	0.74	0.67	0.72	0.135	0.53	0.002	0.08
d 14 wt, kg	7.54	7.45	7.41	7.59	7.49	7.51	0.923	0.63	0.33	0.89
Phase 2 (d 14 to d 28)										
ADG, kg/d	0.45	0.46	0.46	0.46	0.45	0.47	0.048	0.26	0.52	0.12
ADFI, kg/d	6.25	6.12	6.18	6.19	6.07	6.30	0.623	0.33	0.90	0.07
Gain:Feed	0.73	0.77	0.74	0.76	0.76	0.74	0.110	0.05	0.29	0.40
d 28 wt, kg	13.89	13.96	13.79	14.06	13.80	14.04	1.40	0.82	0.34	0.40
Phase 3 (d 28 to d 42)										
ADG, kg/d	0.63	0.65	0.64	0.64	0.65	0.64	0.058	0.08	0.86	0.73
ADFI, kg/d	10.72	10.36	10.51	10.57	10.52	10.56	1.156	0.15	0.78	0.85
Gain:Feed	0.59	0.63	0.61	0.60	0.61	0.61	0.034	0.001	0.19	0.92
d 42 wt, kg	22.75	23.15	22.81	23.09	22.84	23.06	1.948	0.32	0.49	0.59
Phase 4 (d 42 to d 56)										
ADG, kg/d	0.84	0.88	0.87	0.86	0.87	0.86	0.063	0.003	0.25	0.58
ADFI, kg/d	15.75	14.40	15.21	14.94	14.94	15.21	1.683	0.002	0.45	0.43
Gain:Feed	0.54	0.62	0.58	0.58	0.59	0.57	0.059	0.001	0.95	0.13
d 56 wt, kg	34.58	35.53	35.02	35.08	34.99	35.11	2.416	0.06	0.90	0.82
Overall (d 0 to d 56)										
ADG, kg/d	0.45	0.47	0.46	0.46	0.46	0.46	0.133	0.58	0.98	0.82
ADFI, kg/d	9.44	8.93	9.19	9.17	9.10	9.27	0.818	0.003	0.91	0.31
Gain:Feed	0.47	0.52	0.49	0.50	0.49	0.50	0.141	0.13	0.98	0.85

[a] Data represents 48 of 72 planned observations for diet, 16 of 24 planned observations for storage, and 48 of 72 planned observations for sex.

Table 3. Effects of diet, manure storage type, and sex on grow-finish performance (preliminary data)[a].

	Diet		Storage		Sex			P Values		
Main Effects	Control	LNE	Deep Pit	Pull Plug	Barrows	Gilts	MSE	Diet	Storage	Sex
d 56 wt, kg	34.58	35.53	35.02	35.08	34.99	35.11	2.416	0.06	0.90	0.82
Grower 1 (d 56 – 84)										
ADG, kg/d	0.93	0.91	0.92	0.92	0.94	0.90	0.069	0.30	0.63	0.006
ADFI, kg/d	20.39	18.42	19.30	19.51	19.46	19.36	2.521	0.003	0.69	0.87
Gain:Feed	0.46	0.50	0.48	0.47	0.48	0.47	0.071	0.003	0.44	0.35
d 84 wt, kg	60.68	61.09	60.82	60.95	61.38	60.39	3.377	0.55	0.85	0.15
Grower 2 (d 84 -112)										
ADG, kg/d	0.97	1.08	1.03	1.02	1.04	1.01	0.145	0.002	0.67	0.28
ADFI, kg/d	27.19	26.01	27.18	26.01	27.16	26.04	2.359	0.02	0.02	0.03
Gain:Feed	0.35	0.41	0.38	0.39	0.38	0.39	0.066	0.001	0.37	0.58
d 112 wt, kg	88.01	91.36	89.69	89.69	91.07	88.30	4.213	0.002	1.00	0.002
Finisher 1 (d 112 – 140)										
ADG, kg/d	1.05	1.08	1.06	1.07	1.09	1.04	0.231	0.29	0.78	0.24
ADFI, kg/d	29.88	28.60	29.40	29.08	29.60	28.88	3.546	0.08	0.67	0.33
Gain:Feed	0.34	0.37	0.35	0.35	0.35	0.35	0.045	0.006	0.80	0.62
d 140 wt, kg	114.75	119.02	116.69	117.09	118.85	114.93	5.262	0.001	0.71	0.004
Finisher 2 (d 140 – 152)										
ADG, kg/d	0.81	0.81	0.83	0.79	0.80	0.82	0.265	0.93	0.52	0.84
ADFI, kg/d	32.44	29.27	31.02	30.69	31.39	30.32	4.530	0.009	0.72	0.25
Gain:Feed	0.25	0.27	0.26	0.25	0.25	0.26	0.079	0.15	0.51	0.32
d 152 wt, kg[b]	125.68	130.64	128.44	127.88	129.73	126.59	6.237	0.001	0.71	0.04

[a] Data represents 48 of 72 planned observations for diet, 16 of 24 planned observations for storage, and 48 of 72 planned observations for sex.

[b] Data represents 36 of 72 planned observations for diet, 12 of 24 planned observations for storage, and 48 of 72 planned observations for sex.

Table 4. Effects of diet, manure storage type, and sex on ultrasound backfat and loin eye area scans of grow-finish pigs (preliminary data)[a].

	Diet		Storage		Sex			P Values		
Main Effects	Control	LNE	Deep Pit	Pull Plug	Barrows	Gilts	MSE	Diet	Storage	Sex
Grower 1, d 56										
Loin eye area, cm^2	13.82	14.52	14.17	14.17	13.86	14.48	1.907	0.08	0.99	0.12
Backfat, mm	8.01	8.85	8.29	8.57	8.59	8.26	1.089	0.003	0.20	0.14
Grower 2, d 84										
Loin eye area, cm^2	21.81	22.19	22.28	21.72	21.47	22.52	3.276	0.57	0.41	0.12
Backfat, mm	9.50	11.07	10.16	10.41	10.47	10.10	2.617	0.004	0.64	0.49
Finisher 1, d 112										
Loin eye area, cm^2	31.29	31.73	31.95	31.08	31.32	31.70	3.372	0.52	0.21	0.58
Backfat, mm	13.40	14.96	13.90	14.45	15.16	13.19	1.844	0.001	0.15	0.001
Finisher 2, d 140										
Loin eye area, cm^2	34.80	36.16	36.01	34.95	35.61	35.34	2.733	0.04	0.11	0.68
Backfat, mm	16.33	18.63	17.50	17.47	19.44	15.52	2.709	0.006	0.96	0.001
Market, d 152[b]										
Loin eye area, cm^2	37.68	39.42	39.11	37.99	38.15	38.95	2.550	0.005	0.07	0.19
Backfat, mm	18.06	20.95	19.59	19.41	21.49	17.51	2.843	0.001	0.79	0.001

[a] Data represents 48 of 72 planned observations for diet, 16 of 24 planned observations for storage, and 48 of 72 planned observations for sex.

[b] Data represents 36 of 72 planned observations for diet, 12 of 24 planned observations for storage, and 48 of 72 planned observations for sex.

Table 5. Effects of diet, manure storage type, and sex on slaughtered carcass characteristics of finishing pigs (preliminary data)[a].

	Diet		Storage		Sex			P Values		
Main Effects	Control	LNE	Deep Pit	Pull Plug	Barrows	Gilts	MSE	Diet	Storage	Sex
Backfat depth, mm	21.66	23.69	22.57	22.78	24.69	20.66	2.308	0.001	0.66	0.001
Loin depth, cm	6.55	6.52	6.57	6.50	6.51	6.56	0.242	0.57	0.16	0.32
Lean, %	53.80	53.24	53.61	53.43	52.98	54.06	0.629	0.001	0.18	0.001
Base meat price, $/kg	1.27	1.25	1.26	1.26	1.26	1.27	0.108	0.29	0.92	0.58
Carcass grade premium, $/kg	0.11	0.10	0.11	0.10	0.09	0.12	0.022	0.003	0.09	0.001
Carcass value, $/kg	1.39	1.35	1.37	1.37	1.35	1.39	0.111	0.11	0.79	0.05
Hot carcass wt, kg	93.13	96.72	95.13	94.72	96.40	93.45	4.612	0.003	0.66	0.002
Live value, $/kg	1.03	1.01	1.02	1.01	1.00	1.03	0.083	0.16	0.47	0.05
Yield, %	74.00	74.31	74.61	73.69	73.97	74.34	1.833	0.41	0.02	0.32
Total carcass value, $[b]	129.03	130.36	130.24	129.15	129.54	129.86	9.855	0.51	0.59	0.87

[a] Data represents 48 of 72 planned observations for diet, 16 of 24 planned observations for storage, and 48 of 72 planned observations for sex.

[b] Total carcass value ($) = Carcass grade premium ($/kg) * Hot carcass wt (kg).

Table 6. Effects of diet and manure storage type on air concentration data in a wean-finish confinement building (preliminary data)[a].

	Diet		Strorage			P Values	
Gas Concentrations	Control	LNE	Deep Pit	Pull Plug	MSE	Diet	Storage
NH_4 (PSA), ppm	6.6	5.7	6.4	6.0	3.52	0.001	0.005
H_2S, ppb	136.1	142.1	139.4	138.8	286.63	0.65	0.96
SO_2, ppb	11.1	11.5	9.9	12.7	32.89	0.81	0.07
CO_2 (PSA), ppm	1308.3	1312.5	1318.0	1302.8	353.87	0.86	0.33
CH_4, ppb	10.5	10.4	11.5	9.4	6.37	0.83	0.001

[a] Data represents 8 of 12 planned observations for diet and storage.

Table 7. Effect of week of production on air concentration data in a wean-finish confinement building (preliminary data)[a].

Dietary phase:	Nursery	Grower 1	Grower 2	Finisher 1	Finisher 2		P Values
Week of production:	4	8	12	16	20	MSE	Wk of Production
Gas concentrations							
NH_4 (PSA), ppm	3.4	6.6	8.6	6.1	6.3	3.52	0.001
H_2S, ppb	56.9	171.2	143.9	179.9	149.5	286.63	0.001
SO_2, ppb	9.9	14.1	13.3	11.2	8.3	32.89	0.24
CO_2 (PSA), ppm	1424.7	1311.5	1393.7	1157.5	1231.5	353.87	0.001
CH_4, ppb	7.2	11.4	13.0	10.2	10.7	6.37	0.001

[a] Data represents 16 of 24 planned observations for wk of production.

Estimating Annual NH_3 Emissions from U.S. Broiler Facilities

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Abstract

Recently, several U.S.-based research projects have been completed to acquire ammonia emissions baseline data for broiler housing (Wheeler et al., 2004, 2006; Burns et al., 2003) and layer housing (Liang et al., 2005). The issue of estimating these operations' contribution to an annual ammonia emission budget needs to be resolved. For the case of layer houses, ammonia emission is strongly impacted by the nature of manure management within the building, with emissions from high-rise facilities typically an order of magnitude greater than those from manure-belt facilities. Thus, for a layer facility the use of a standard emission factor (EF) is not unreasonable, provided that the factor reasonably takes into account the parameters which influence emission rate, namely temperature, ventilation rate, number, size and age of birds, etc).

Production facilities in which poultry or animals grow rapidly, i.e. "meat-type" animals, present a completely new challenge to standard methods for estimating emissions. For example, broiler operations are uniquely different than layer operations, because the birds are grown from day-old to market weight. While consumer demand drives the specific mature weight of a "broiler (from "Cornish hens" weighing 1 kg to "roasters" weighing 4 kg), the fact remains that building emission rate changes with bird size. Integrating this variable emission rate over an entire year is the ideal means of estimating the annual contribution to an ammonia emission inventory. Conceptually, one could estimate a mean daily emission rate, expressed for example as (g NH_3 $bird^{-1}$ day^{-1}), or (kg NH_3 $house^{-1}$ day^{-1}), and then multiply by the number of days per year in which birds are present in a facility. This approach requires knowledge of number of flocks grown per year, mature weight of each flock, and down-time between flocks.

We have a developed an alternative emissions estimate (Gates et al., 2005), using results from the recently completed U.S. broiler emission project (Wheeler et al, 2004, 2006). Emission rate increases in a linear relationship with flock age from near zero at the start of the flock to a maximum at the end, 28 to 63 days later.

An estimate of daily NH_3 emissions per bird (±std. dev.) from these data is thus:

$$ER_b = 0.031(\pm 0.0057)\cdot x,\ where\, x = \left\{ \frac{age, \qquad if\, used\, litter}{0, if 1 < age < 6; age - 6, if\, new litter} \right. \tag{1}$$

where

ER_b = emissions rate, g NH_3 $bird^{-1}$ d^{-1}
age = bird age, d

On a typical broiler farm, five to eight flocks (per house) are grown annually depending on finished bird weight and market demand. The houses are empty for seven to fourteen days between flocks while cleaning and maintenance is accomplished. Production houses may be empty for a further fourteen to twenty-one days to allow for annual maintenance and litter removal. We present a model that takes into account; broiler market weight, numbers slaughtered and ammonia emissions to compute annual emissions estimates. The method can be readily applied and should provide for a more accurate annual budget estimate than is currently available. In addition, because the slope in equation (1) has a known standard error (i.e. 0.0057 g NH_3 bird^{-1} d^{-2}), we can assess the impacts of a) fresh litter vs. re-used litter, b) number of flocks per year and market weight of birds, which can vary between flocks, and c) uncertainty in emission estimates.

The model was used to evaluate some of these effects, using a typical Kentucky broiler house (12m x 150m). Interestingly, the annual emission rate was less for broilers (28,000 birds per flock, 2.1 kg mature weight @40 d) than for heavy broilers (24,000 birds per flock, 2.45 kg mature weight @49 d) or for roasters (18,000 birds per flock, 3.25 kg mature weight @63 d), 3,786, 4,219 4,473 kg NH_3 house^{-1} yr^{-1} respectively (new litter). This can be explained by the fact that while fewer birds were raised in the houses with larger market weights (5.2, 6.7 and 7 flocks per year), there are more days with older birds. Another interesting finding was that the effect of new versus re-used litter was substantial (27%, 37% and 47% potential reduction for broiler, heavy broiler and roaster birds, respectively). Unfortunately, this potential for reduction occurs at a heavy price, namely a 5 to 10-fold increase in litter costs, a 5 to 7-fold increase in litter volume to handle and appropriately dispose, and a substantially reduced fertilizer value.

Application of a reasonable prediction interval on these estimates was performed by adjusting the slope in equation (1) by ±3 standard errors, as depicted graphically in Figure 1. This demonstrates the variable nature of emissions estimates, and with annual emission (the end-point for each curve) for broiler, heavy broiler and roaster facilities ranging from 3,420, 3,811, and 4,040 kg NH_3 house^{-1} yr^{-1} respectively (new litter), with similar differences determined for new versus re-used litter.

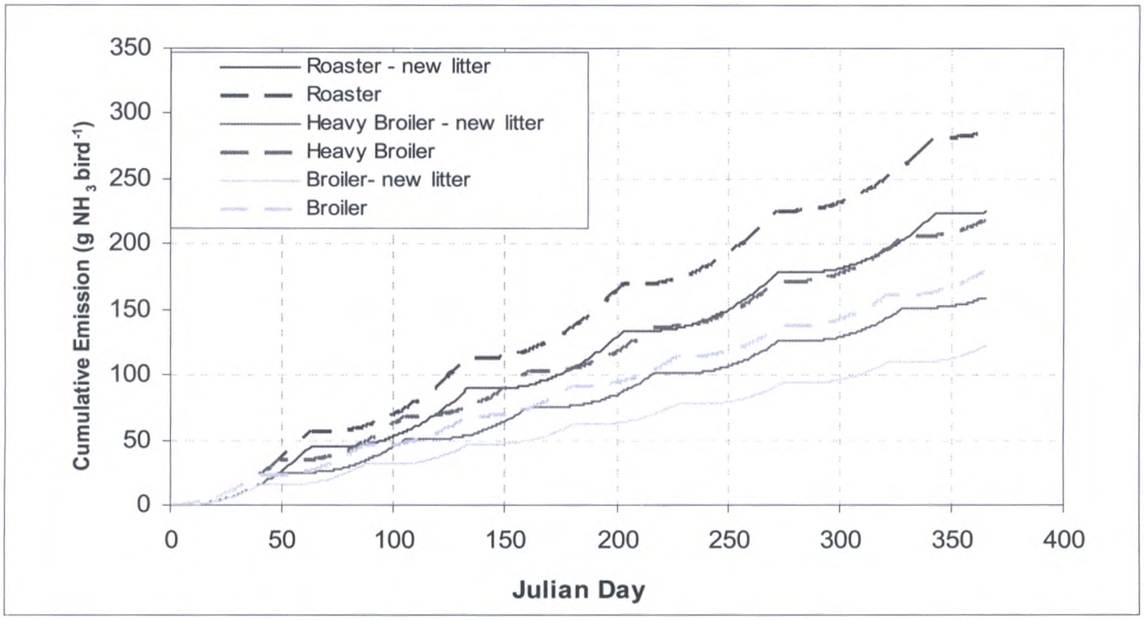

Figure 1. Cumulative ammonia emission over a year, from multiple flocks, for roaster, heavy broiler or broilers, and new vs. re-used litter, assuming mean ER – 3 SE_{ER} as per Equation 1

The broiler emission inventory model was used to estimate annual emission from Commonwealth of Kentucky broiler facilities, using USDA's National Agricultural Statistics Service data for 2002. The predicted emission ranges from 8,844 to 11,696 metric tons for new and re-used litter, respectively. This compares with the current EPA National Emission Inventory estimate of 664,238 metric tons NH_3 in 2002. For this time period, Kentucky production was about 3.2% of national production, and if we assume a proportional contribution to national emission inventory, this is 21,255 metric tons. This clear discrepancy between the model predictions and current EPA estimates (a factor of 2 to 3) suggests a need to refine the national inventory estimates in the case of meat-type animals.

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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 CO_2 (+ $^{13}CO_2$), CH_4, N_2O, NH_3 and H_2O (+ 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 CO_2, N_2O, CH_4 and H_2O exchange including isotopic fractionations in CO_2 and H_2O 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 CO_2, CH_4, N_2O, CO and water vapour. Isotopic species $^{13}CO_2$ and HDO can also be determined, providing a method for real-time field measurements of $\delta^{13}C$ in CO_2 and δD in H_2O. 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 (N_2O) as the tracer because it is safe and can be determined accurately at low levels by FTIR at a release rate of ca. 10g hr^{-1} or 240 g day^{-1} per head. The cattle are free to graze normally in ca. 50 x 50 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

$$F(CH_4) = F(N_2O) \cdot \frac{C_{CH_4}}{C_{N_2O}}$$

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.

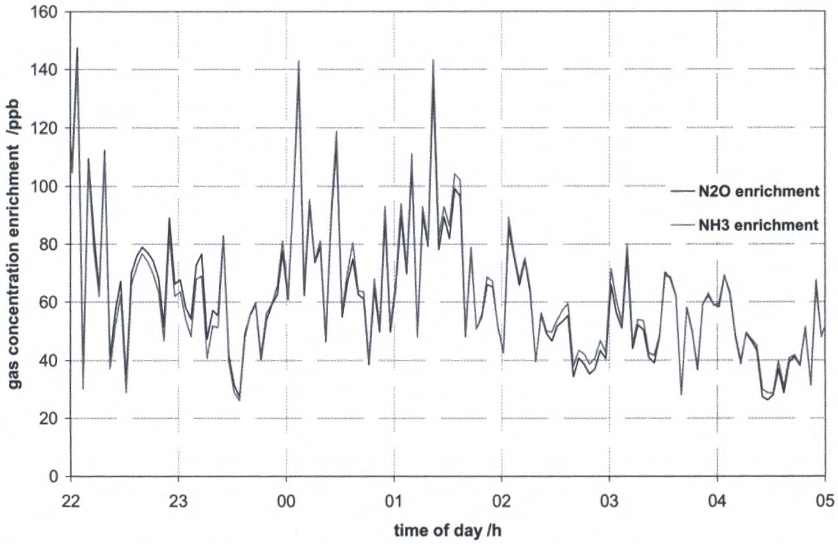

Figure 1. Concentrations of N_2O and NH_3 measured over an open path 100m downwind of controlled releases of 5 std L min^{-1} of each gas. These measurements demonstrate that to a very good extent the gases remain well mixed when released from the same location.

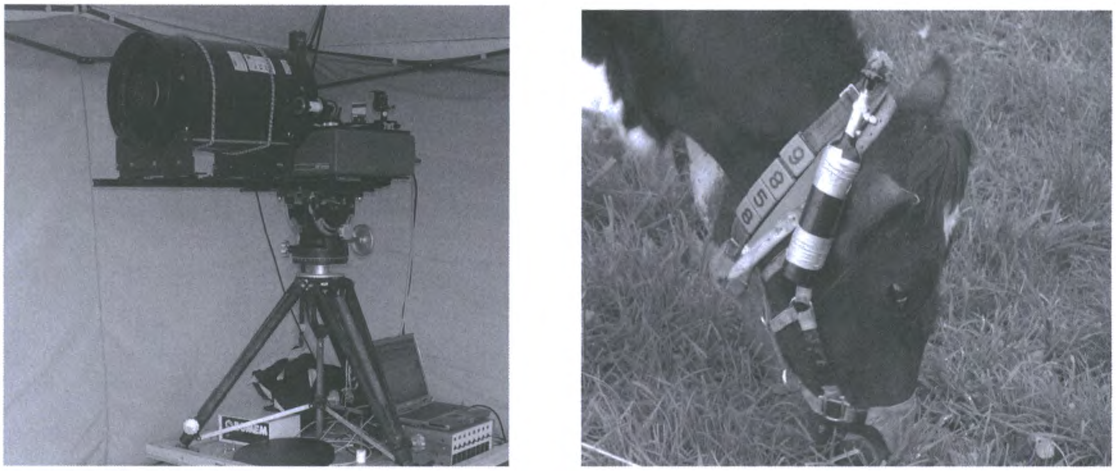

Figure 2. The open path FTIR spectrometer (left) and tracer release canister mounted on a grazing cow (right)

Surface-Atmosphere Exchange of Trace Gases
Field Measurements of δD in Water Vapour and $\delta^{13}C$ 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 HDO/H_2O ratio in water vapour and $\delta^{13}C$ 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.

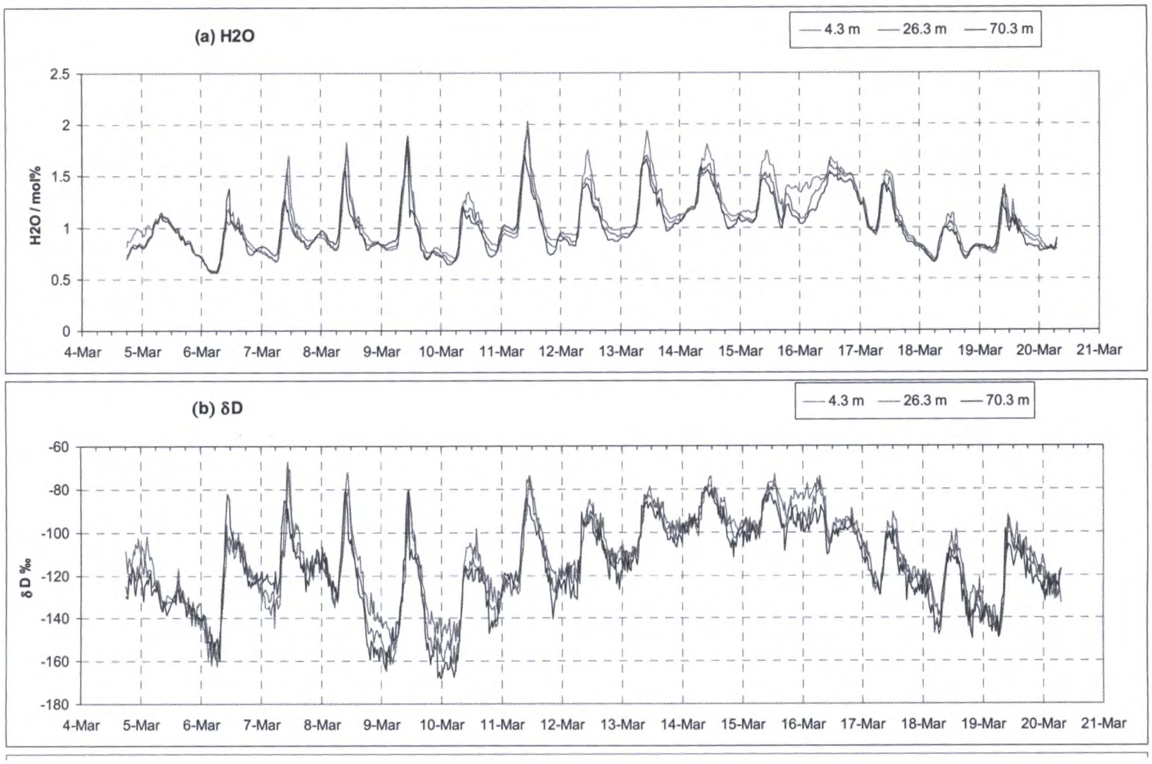

Figure 3. Continuous vertical profiles of water vapour concentration (upper) and deuterium fractionation δD in H_2O (lower) over two weeks in a 40 m eucalypt forest

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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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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 inteferometer 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 Schauberger, 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

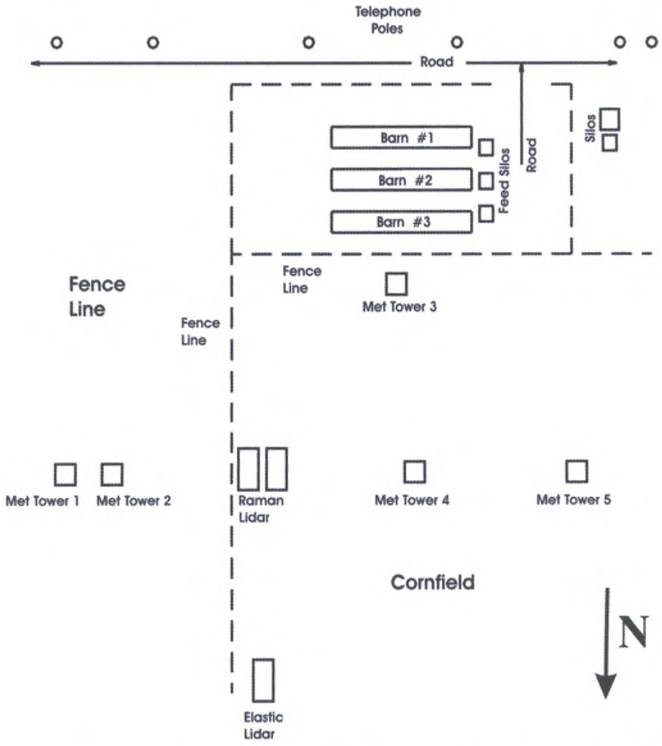


Figure 1. The schematic layout of the experiment

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 Moulsley, 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.

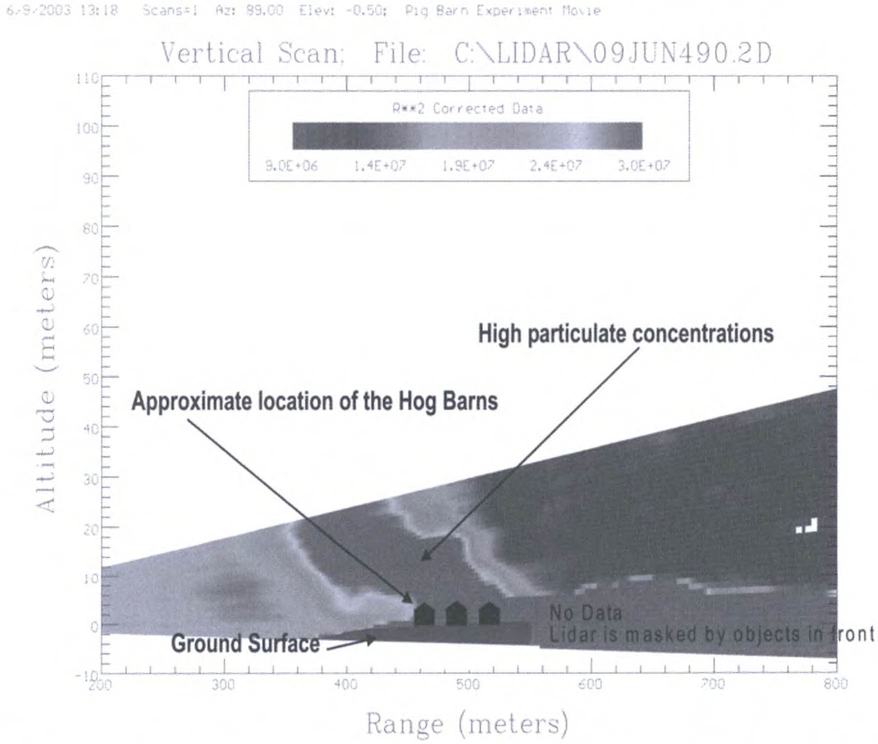


Figure 3. A lidar scan showing the relative particulate concentrations in a vertical slice through the atmosphere. The location of the ground surface and the three barns has been added to show their location. Blue colors indicate regions of low particulate concentration and reds indicate areas of high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

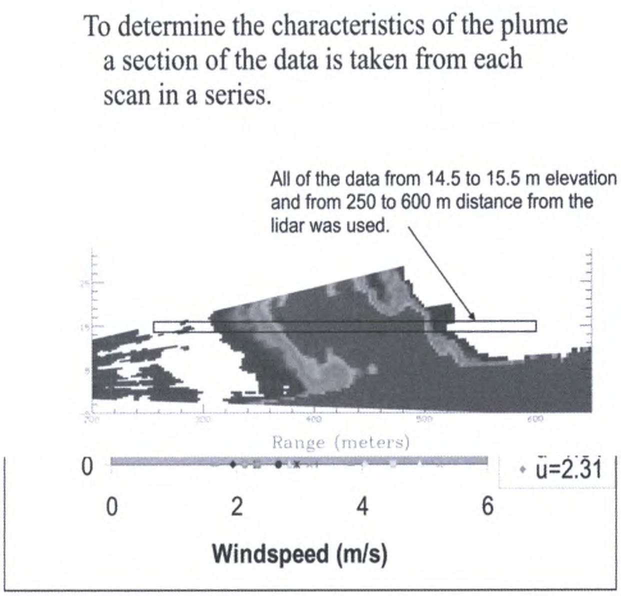
Before collecting data with the miniature elastic lidar and the Raman lidar, distances from the two-lidar systems relative to the hog barns were measured with the miniature elastic lidar. The physical path length from the miniature elastic lidar to the hog confinement barns was approximately 500m. Measurements 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.

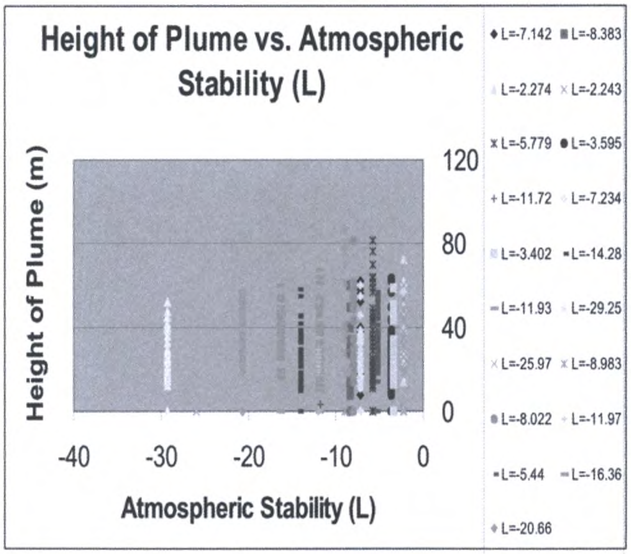


To determine the characteristics of the plume a section of the data is taken from each scan in a series.

All of the data from 14.5 to 15.5 m elevation and from 250 to 600 m distance from the lidar was used.

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.

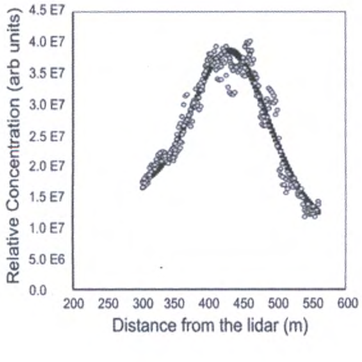


Figure 8. A plot the data from a puff plotted against its fitted function of the form shown above the figure

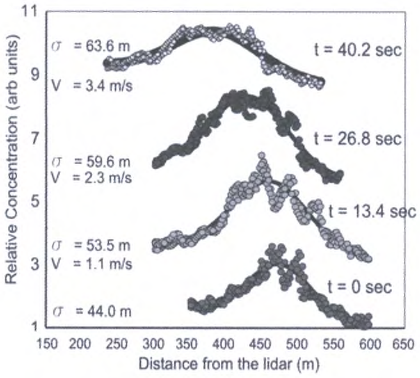
The rate of growth of the plume was studied by taking cross sections through the puffs at a constant height. After the plume has detached from the barns, all of the data from a narrow altitude band is used to fit a Gaussian function modified to account for the fact that the air upwind is cleaner than 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 develop that are robust enough to handle typical environmental conditions at AFOs (i.e., warm humid and dusty), while at the same time being able 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 Teldar 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 (Aglient Technologies) and PFPD (OI Analytical, College Station, TX)) connected in parallel. The column effluent was split using an Agilent mirofluidic 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; methanelthiol: 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 Response Factor (pmol S/area)	r^2	MSD Inert Response Factor (pmol S/area)	r^2
Hydrogen sulfide	3.12×10^4	0.984	9.13×10^1	0.999
Carbonyl Sulfide	2.51×10^4	0.994	1.54×10^2	0.997
Methyl Mercaptan	2.20×10^4	0.991	1.14×10^2	0.993
Carbon Disulfide	4.23×10^4	0.967	1.52×10^3	0.998

Table 3. Determination of VSCs concentration in air at AFO

Producer Facility	Location	H_2S[a]	COS[b]	Carbon Disulfide	Methyl Mercaptan	DMS[c]	DMDS[d]	DMTS[e]
		Analyte concentration in air (ppbv)						
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 Tunnel	2.3	ND	1.7	2.0	4.3	14	0.6
	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

[a]H_2S, hydrogen sulfide; [b]COS, carbonyl sulfide; [c]DMS dimethyl sulfide; [d]DMDS, dimethyl disulfide; [e]DMTS, dimethyl trisulfide; [f]ND, 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 compared 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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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.

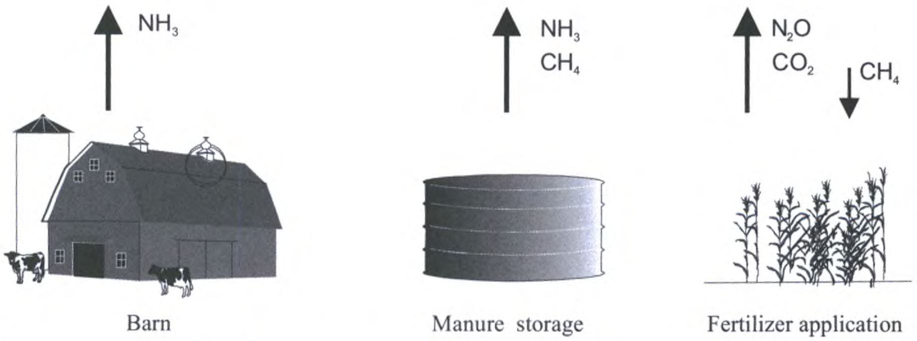

Figure 1. Main gas fluxes during agricultural operations

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) CO_2 - balance method and C) tracer gases (SF_6 or Krypton 85).

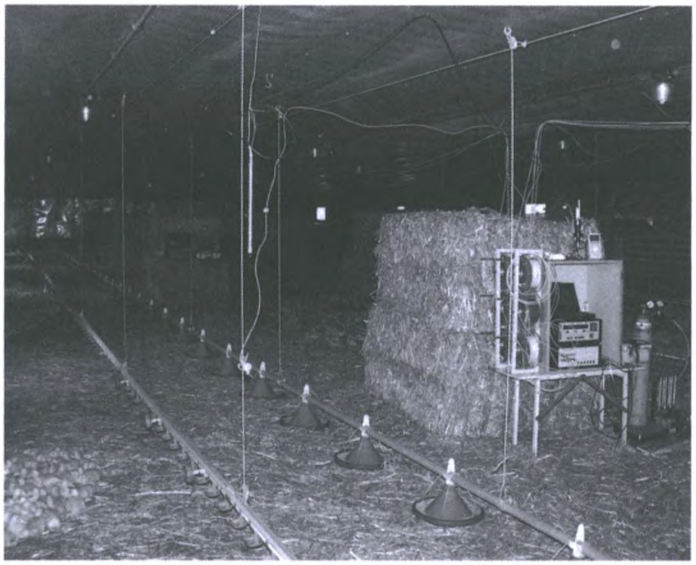

Figure 2. Equipment for gas analyses and gravimetric tracergas dosing in a forced ventilated poultry house

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 mtabolism) and mainly only available as averaged data of a day. So it is important to validate animal data under recent production conditions. Additional 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.

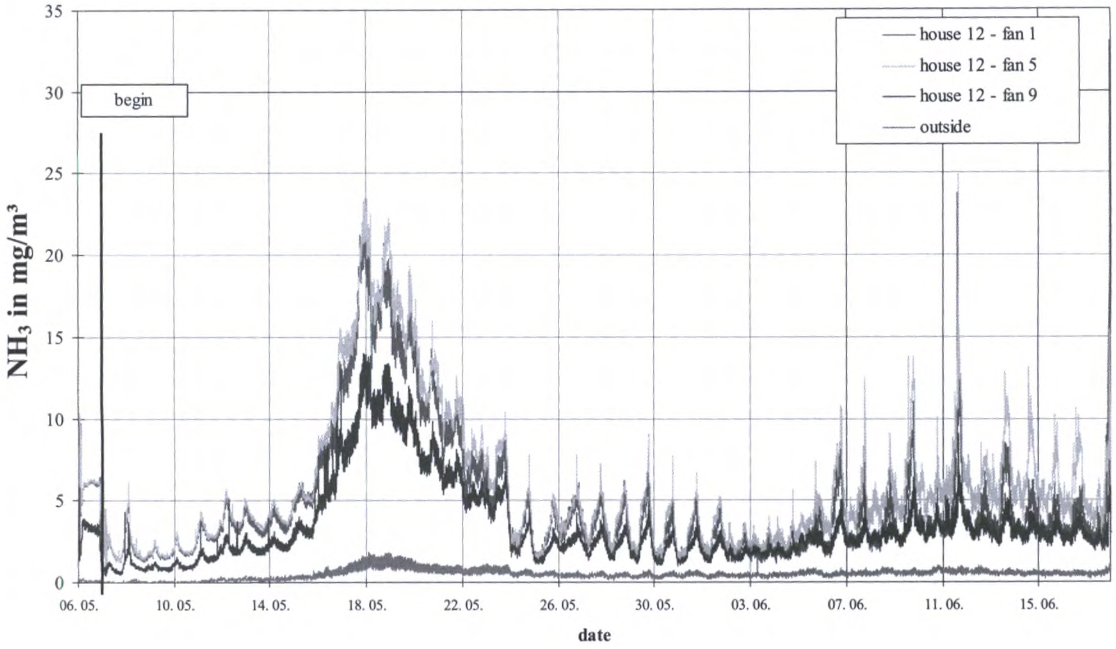

Figure 3. Ammonia concentration in exhaust air at different fans (springtime fattening period of chickens)

Table 1: Ammonium emission stream (g/year per laying hen) determined by SF_6 – and CO_2 – 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.

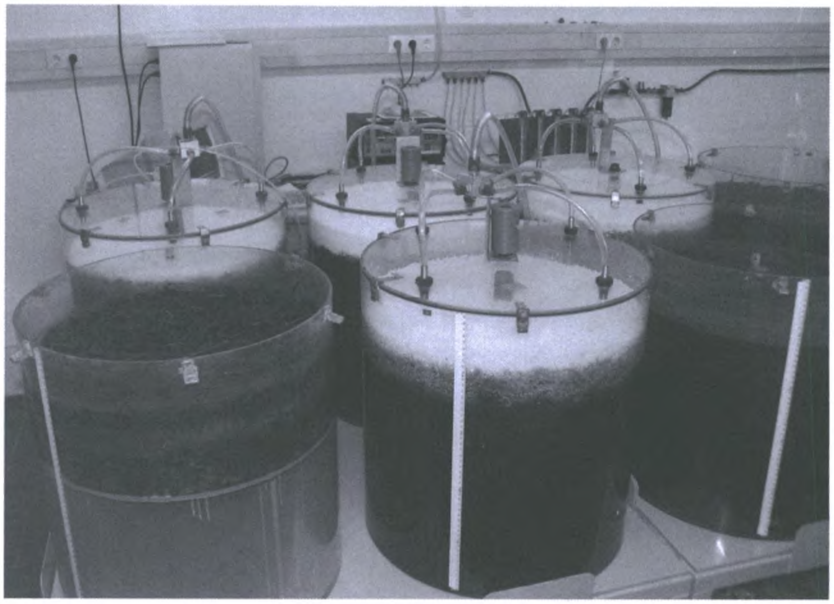

Figure 4. Measurement of gaseous emissions from manure storage facilities with dynamic chambers on lab scale

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.

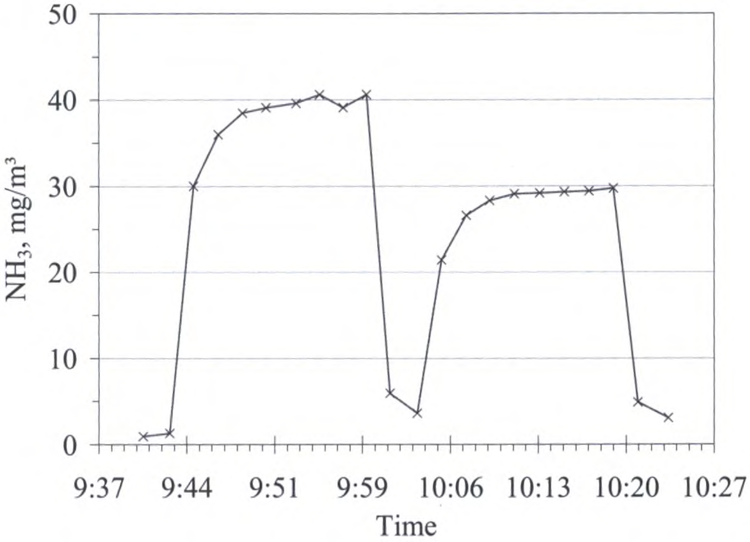

Figure 5. Increase of NH_3 in dynamic chambers for manure storage.

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

Measurements of emissions of CO_2, CH_4, N_2O and NH_3 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 m^3 and area 0.292 m^2; 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 CO_2 concentration was used as a reference. The results showed that a linear approximation could be applied over a period of at least 10 min.

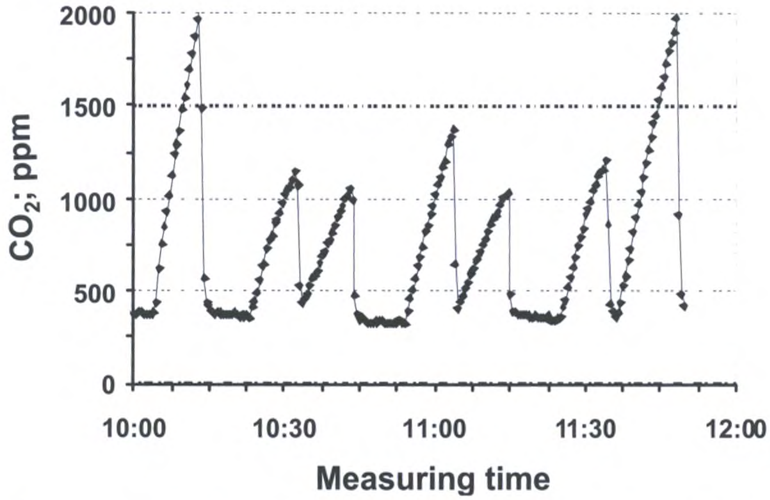

Figure 7. Increase of CO_2 in a gas flux chamber on windrows of animal waste, measured with multigas monitor

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 CH_4, CO_2 and N_2O. 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 NH_3-measurements doubles approximately for low concentrations (below 5 ppm) due to the high mobility and extraordinary absorbability and diffusion of NH_3 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 $C(t) = C_0 (1 - b * t)$ was obtained. For CH_4 and CO_2 the coefficient b is 0.0039 h^{-1} and for N_2O and NH_3 b it is 0.0086 h^{-1}. After a storage time of 6 hours (or up to 24 hours), the concentration of CH_4 and CO_2 dropped by about 2.5% (approx. 10% after 24 h) and in case of N_2O and NH_3 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 CO_2 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.