Table 3: CO_2 emissions from different soils

*Soil type**	Index of soil productivity	mg C-CO_2 kg within 14 days	tons C-CO_2 ha^{-1} within growing season	C-CO_2 thousend tons from total area of soils within growing season
Fluvisols and Calcaric Fluvisols	34-95	86.4-33.4 (59.9)	3.78	1 710
Mollic Fluvisols and Calcaric Mollic Fluvisols	52-100	79.4-21.0 (50.2)	3.44	644
Calcaric Haplic Chernozems	67-96	71.8-31.0 (51.4)	3.52	525
Haplic Chernozems and Luvi-Haplic Chernozems	60-93	76.0-37.7 (56.8)	4.03	677
Haplic Luvisols and Albi-Haplic Luvisols	48-90	80.9-43.7 (62.3)	4.45	1 348
Albic Luvisols and Stagnic Glossisols	26-66	91.1-72.5 (81.8)	5.01	254
Planosols and Stagnosols	25-50	91.8-80.2 (86.0)	5.05	883
Cambisols and Umbrisols	15-50	101.3-80.2 (90.7)	4.95	3 475
Rendzic Leptosols	13-40	103.8-83.8 (93.8)	4.43	505
Podzols	3-10	119.6-107.9 (113.7)	5.17	15
Solonchaks and Solonetz	5-10	115.9-107.9 (111.9)	5.09	25

* WRB 1998

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Measurement and Modeling of Hydrogen Sulfide Emissions Across the Gas-Liquid Interface of an Anaerobic Swine Waste Treatment Lagoon

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Abstract

Hydrogen sulfide (H_2S) is a colorless gas emitted during decomposition of hog manure that produces an offensive "rotten egg" smell and is considered a toxic manure gas. In the southeastern US, anaerobic waste treatment lagoons are widely used to store and treat hog excreta at commercial hog farms. Environmental concerns and complaints regarding air and water quality associated with the increased number of animals and management of subsequent wastes accompanying the growth of this industry has been considerable. However, due to a lack of intensive measurement initiatives, emissions of hydrogen sulfide from anaerobic waste treatment lagoons have not been well quantified.

Under anaerobic conditions, any excreted sulfur that is not in the form of H_2S (i.e., certain amino acids) will be reduced microbially to produce H_2S and so manures managed as liquids or slurries are potential sources of hydrogen sulfide emissions. The magnitude of H_2S emissions in this type of environment is a function of liquid phase concentration, temperature, pH and meteorological parameters. In aqueous form, H_2S exists in equilibrium with the bisulfide anion (HS^-) and sulfide anion (S^{2-}). Temperature and pH affect the solubility of H_2S in water. As pH shifts from alkaline to acidic (pH<7), the potential for H_2S emissions increases.

The process of hydrogen sulfide emissions from anaerobic waste treatment lagoons are investigated using a Coupled Mass Transfer with Chemical Reactions Model. This model is based on the concept of simultaneous mass transfer and equilibrium chemical reactions. Both aqueous phase and gas phase reactions are considered. A sensitivity analysis was performed and model results were compared with hydrogen sulfide fluxes measured at a commercial swine finishing farm waste treatment storage lagoon in North Carolina using a dynamic emission flux chamber system. The measurements were made continuously for ~5 day increments over all four seasons such that diurnal and seasonal variations were established. Experimental results will be utilized to evaluate the model's accuracy in calculating lagoon hydrogen sulfide emissions.

Introduction

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 concentrations greater than 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.

Once released into the atmosphere, hydrogen sulfide reacts with the hydroxyl radical, OH, oxidizing to form sulfur dioxide (SO_2). Sulfur dioxide then undergoes a series of photochemical reactions, and may eventually form sulfuric acid (H_2SO_4). Such atmospheric gas phase reactions may lead to the formation of condensable products that associate with the atmospheric aerosol, e.g., gaseous H_2SO_4 may be neutralized by ammonia to form sulfate salts (Warneck, 2000). Aerosols such as ammonium sulfate may transport and deposit downwind of its source, possibly leading to nitrogen overloading and associated environmental problems such as enhanced eutrophication in sensitive river/coastal ecosystems and soil acidification, which may in turn upset plant nutrient balances near sources (Paerl, 1997).

To date, few studies have reported H_2S emissions from waste storage treatment lagoons (Zahn et al., 2002; Lim et al., 2003). Arogo et al. (2000) studied the concentration and production of hydrogen sulfide from stored liquid in a laboratory experiment. Arogo et al. (1999) have investigated the effects of environmental parameters (wind speed and air temperature) and manure properties (solids content and liquid temperature) and developed a mass transfer coefficient for emission of hydrogen sulfide from liquid swine manure.

Over the last few years, changes in livestock production methods in the U.S. have led to the emergence of large-scale commercial livestock operations, substantially increasing the number of animals in geographically concentrated areas (Aneja et al., 2006). As emissions of trace gases (i.e., nitrogen and sulfur species) likely increase in parallel with the growth and consolidation of this industry, it is important to ensure that these operations do not exceed state regulatory levels for gases such as hydrogen sulfide.

In this study, a Coupled Mass Transfer and Chemical Reactions Model based on the concept of simultaneous mass transfer and equilibrium chemical reaction is used to predict the rates of hydrogen sulfide emission from swine waste storage and treatment lagoons. A field experiment was previously conducted at a commercial swine finishing operation in North Carolina. These experimental results, along with values reported in the literature, are used to evaluate the model's accuracy in calculating lagoon hydrogen sulfide emissions.

Model and Field Experimental Methods

Experimental Flux Measurements

Hydrogen sulfide flux measurements were made at a commercial swine finishing operation in eastern North Carolina. The waste from the animal confinement houses was flushed out with recycled lagoon effluent and discharged into the anaerobic lagoon from each house approximately once per week (varying days for each house).

Hydrogen sulfide flux was measured using a dynamic flow through chamber system (Aneja et al., 2000), consisting of a fluorinated ethylene propylene (FEP) Teflon-lined open bottom cylinder inserted into a floating platform. When the platform and chamber system were placed at a randomly chosen location on the lagoon, the chamber penetrated the lagoon surface to a depth of 6-7 cm, thus forming a seal between the lagoon surface and the air inside the chamber. Compressed zero-grade air was pumped through the chamber at a known flow rate and the air inside the chamber was continuously stirred by a motor driven Teflon impeller. Once the chamber reached steady-state conditions, samples were drawn through Teflon tubes to a Thermo Environmental Instruments (TEI) Model 450C pulsed fluorescence H_2S/SO_2 analyzer where the volumetric concentration was measured.

Continuous measurements were made for about a one-week period during four seasons, beginning October 2004 and ending June 2005, in order to determine seasonal trends. A Model CSIM11 pH probe and a CS107 temperature probe (Campbell Scientific Inc., Logan, UT) were submerged in the lagoon at a depth of ~6-7cm beneath the surface in order to continuously monitor near-surface lagoon pH and lagoon temperatures.

Lagoon Sample Collection

To determine the concentration of total sulfide samples in the slurry, liquid samples were collected from the lagoon surface 1-2 times per day during the flux experiment. Lagoon samples collected were preserved with 6N sodium hydroxide and 2N zinc acetate to pH > 9, according to North Carolina Division of Water Quality (NC DWQ) specifications.

Aqueous hydrogen sulfide exists in equilibrium with the hydrogen sulfide anion (HS^-) and the sulfide anion (S^{2-}) and all three comprise total sulfide. Once total sulfide (C_{TS}) concentration has been determined, the bulk dissolved hydrogen sulfide, which is a function of C_{TS}, pH, and lagoon temperature (T_L), can then be calculated. Snoeyink and Jenkins (1980) determined the relationship for the fraction of sulfide species (H_2S, HS^-, S^{2-}) present in aqueous solution as a function of pH and estimated the aqueous H_2S concentration for known C_{TS} by the following equation:

$$C_{H_2S} = C_{TS}\left(\frac{10^{-pH}}{10^{-pH}+10^{-pKa}}\right) \tag{1}$$

where C_{H2S} and C_{TS} are the concentrations of dissolved hydrogen sulfide and total sulfide, respectively. The acidity constant for hydrogen sulfide, pK_a, is a function of temperature and, based on the Van't Hoff relationship and the standard enthalpy values for H_2S and HS^- (Snoeyink and Jenkins, 1980), can be determined by the following second-order polynomial equation:

$$pK_a = 4.545\text{x}10^{-5} * T_L^{\,2} - 1.504\text{x}10^{-2} * T_L + 7.447 \tag{2}$$

The solubility of H_2S in water increases at pH values above 7 and as pH shifts from alkaline to acidic ($pH < 7$), the potential for H_2S emissions increases. The sulfide anion can form at $pH > 12$, well above the range for a typical hog lagoon, and so it is not expected to be present in the effluent sampled.

For the physiochemical process of H_2S transfer across the gas-liquid interface, the transfer of the aqueous form ($H_2S_{(aq)}$) into the gaseous form ($H_2S_{(g)}$) can be expressed by:

$$H_2S_{(aq)} \rightarrow H_2S_{(g)} \tag{3}$$

Only the $H_2S_{(aq)}$ fraction, not the ionized form (HS^-), can be transferred across the gas-liquid interface (U.S. EPA, 1974).

Mass Transport Model

The mass transport with chemical reactions model is based on the quiescent thin film concept (Whitman, 1923; Danckwerts, 1970). The principle characteristics of this transport model are depicted in Figure 1.

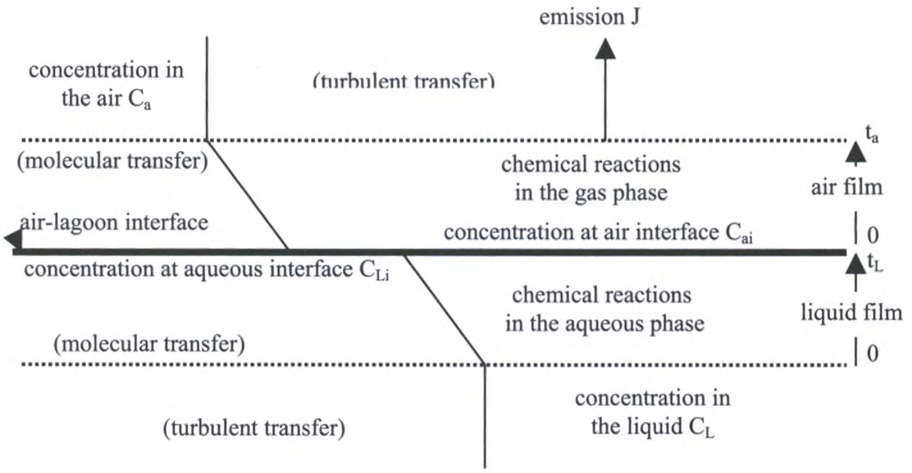

Figure 1. Two film theory of mass transfer

A gas phase film extends upward from the air-liquid interface to the well-mixed air region, and a liquid phase film extends downward from the same interface to the well-mixed liquid region of the lagoon. The film thickness of a given phase was defined as the ratio of the hydrogen sulfide diffusion coefficient for that phase to the mass transfer coefficient as experimentally determined by Mackay and Yeun (1983) for the same phase.

The model explicitly takes into account molecular diffusion and chemical reactions. In the liquid film, only hydrogen sulfide's reversible reaction in water is considered, and pH is assumed constant. Based on these assumptions, a theoretical result of Olander (1960) is used to define the hydrogen sulfide flux, J_i, in the liquid phase at the air-liquid interface:

$$J_i = \left(\frac{D_c}{t_L}\right)\left(C_L - C_{Li}\right)\left(1 + \frac{D_A}{D_c} K_{rL}\right) \tag{4}$$

where A denotes hydrogen sulfide anion [HS^-] and C denotes hydrogen sulfide [H_2S]; D_A and D_c are the diffusivities of hydrogen sulfide anion and hydrogen sulfide, respectively; t_L is the thickness of the liquid film. Hydrogen sulfide concentrations at the interface and in the bulk of the liquid phase are given by C_{Li}

and C_L, respectively. K_{rL} is the overall effective equilibrium constant and is given by $K_{rL} = \frac{K_{H_2S}}{[H^+]}$ in which K_{H_2S} is the dissociation constant for the equilibrium equation of hydrogen sulfide in the liquid.

For the gas phase film, the primary reaction of hydrogen sulfide with the hydroxyl radical [OH] is considered (Seinfeld and Pandis, 1998). In the gas film, [OH] is assumed to have a constant concentration, giving an effective first order reaction for hydrogen sulfide, with first order reaction rate constant in the gas phase, given as

$$k_{ra} = k[\mathrm{OH}] \tag{5}$$

The following equation describes the transport of hydrogen sulfide in the gas phase:

$$D_a\left(\frac{d^2C(z)}{dz^2}\right) = k_{ra} \times C(z) \tag{6}$$

Where C(z) is the hydrogen sulfide concentration at the height of z in a gas film of thickness t_a and D_a is the molecular diffusion of hydrogen sulfide in the gas phase. The boundary conditions are:

$$z = 0;\ C(0) = C_{ai} \tag{7}$$

$$z = t_a;\ C(t_a) = C_a \tag{8}$$

The solution to the mass transport equation results in hydrogen sulfide flux to the atmosphere being expressed in terms of film thickness, gas phase hydrogen sulfide diffusion coefficient, the effective first order rate constant, an the concentrations at the film boundaries.

Assuming the gas phase and liquid phase hydrogen sulfide concentrations at the air-liquid interface are in equilibrium and related by Henry's Law constant (H), Equation 4 can be combined with a gas phase interfacial expression for flux based on the solution to Equation 6. The result is an expression for the flux of hydrogen sulfide from the lagoon water to the atmosphere.

Results

The model reveals that the calculated hydrogen sulfide flux is dependent on several variables, including lagoon temperature, pH, and aqueous hydrogen sulfide content of the lagoon. Lagoon temperature plays a significant role in estimating hydrogen sulfide flux. During model sensitivity analysis, constant values of 7.5, 20.0°C, and 10.0 mg L^{-1} were used for pH, lagoon temperature, and total aqueous sulfide content, respectively. Two values were held constant and one variable altered was in turn to test model performance.

Effects of lagoon temperature include molecular diffusion coefficients in both phases and concentration control through variations of Henry's Law constant and dissociation constant. Measured near-surface lagoon temperature ranged from 9.1 to 32.5°C throughout the year. The model temperature was varied from 2.5 to 40°C.

The chemical equilibrium of the H_2S-HS^- system in aqueous phase is driven by lagoon pH. The pH in the model was varied from 6.5 to 8.5. However, lagoon pH measurements only varied slightly, from 7.8-8.2 and so results from other studies are also used to test the model's sensitivity to this parameter.

The waste from the confinement houses was flushed out with recycled lagoon water and discharged into the lagoon from the top (top-loading). Sulfide 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). During the course of the measurement campaign, the amount of total sulfide in the lagoon ranged from 0.1 to 13.0 mg L^{-1}. The concentration in the model was varied from 0 to 50 mg L^{-1}.

Conclusions

A Coupled Mass Transfer with Chemical Reactions Model was developed in order to accurately predict hydrogen sulfide emission rates from anaerobic waste treatment lagoons. The model reveals that the calculated hydrogen sulfide flux is dependent on several variables, including lagoon temperature, pH, and aqueous hydrogen sulfide content of the lagoon. Model results were compared with field measurements made over the course of a year at a commercial finishing swine farm operating under steady-state conditions.

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Characterization of Non-Methane Volatile Organic Compounds at Five Confined Animal Feeding Operations in North Carolina

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Abstract

Samples were collected and analyzed in a field study to characterize C_2-C_{12} volatile organic compounds (VOCs) emitted at five swine facilities in Eastern North Carolina between April 2002 and March 2003. Two sites employed conventional lagoon and field spray technologies, while three sites utilized various alternative waste treatment technologies in an effort to substantially reduce gaseous compound emissions, odor, and pathogens from these swine facilities. More than 100 compounds, including various paraffins, olefins, aromatics, ethers, alcohols, aldehydes, ketones, halogenated hydrocarbons, phenols, and sulfides were positively identified and quantified by Gas Chromatographic/Flame Ionization Detection (GC/FID) analysis and confirmed by Gas Chromatographic/Mass Spectrometry (GC/MS). GC/MS analysis of one particularly complex sample collected assisted in providing identification and retention times for 17 sulfur type VOCs including dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide as well as many other VOCs. Highest VOC concentration levels measured at each of the facilities were near the hog barn ventilation fans. Total measured VOCs at the hog barns were typically dominated by oxygenated hydrocarbons (HCs), i.e., ethanol, methanol, acetaldehyde, and acetone. These compounds, in addition to other oxygenated VOCs measured at the various sites, generally represented ~37-73% of net total measured VOCs that were emitted from the hog barns at the various sites. Dimethyl sulfide and dimethyl disulfide, both recognized as malodorous compounds, were determined to have higher concentration levels at the barns than the background at every farm sampled with the exception of one farm during the warm sampling season.

Introduction

Swine production has increased dramatically over the last decade in North Carolina, making the state the second largest producer of hogs in the United States, with a population of ~10 million animals (NCDA, 2003). In recent years, contract arrangements for production have aided the expansion of hog operations by providing the capital necessary for swine operations to adopt new technologies and achieve major growth (McBride and Key, 2003). More hogs are confined to smaller areas, thereby increasing amounts of odorous and potentially harmful compounds due to a higher amount of excretion.

In response to environmental concern, the North Carolina Attorney General determined that the development of "Environmentally Superior Technologies" (ESTs) would serve well the public interest of North Carolina, with the objective of reducing potentially hazardous emissions from these swine facility sites (Aneja et al., 2003). Project OPEN (Odors, Pathogens, and Emissions of Nitrogen) was established in December 2000 in an effort to evaluate various alternative waste treatment technologies (i.e., ESTs).

Emissions of compounds such as methane and ammonia from swine facilities have been well documented (McColloch et al., 1998; Sharpe and Harper, 1999; Walker et al., 2000; Aneja et al., 2001; Childers et al., 2001). This study focuses exclusively on the characterization of C_2-C_{12} volatile organic compounds (VOCs) present in the ambient air at various swine facilities located in the eastern region of North Carolina and may be regarded as a survey to determine various gaseous compounds. Some of these compounds are associated with unpleasant odors in this type of rural environment. VOC sample collection strategy was designed to assess VOCs from suspected emission sources at the various potential ESTs and conventional swine farm locations. Samples were collected at the housing areas as well as the technologies (i.e., storage lagoons) at all sites.

VOCs have been reported from several swine farms in Eastern North Carolina to investigate odor complaints (Schiffman et al., 2001a). The compounds detected in this study include various paraffins, olefins, aromatics, ethers, alcohols, aldehydes, ketones, halogenated hydrocarbons, phenols, and sulfides. Sulfides and phenols have long been associated with odor problems at swine facilities (Hammond et al., 1989; O'Neill and Phillips, 1992). Results presented consist of the high C_2-C_{12} VOCs levels observed from the ventilation fans at the hog confinement barns. Concurrently collected samples of background air are included to more clearly determine the VOCs resulting from hog barn activities.

Methods

Experimental Research Site Descriptions

Samples were collected at four different farms and one laboratory site located in Eastern North Carolina. Three sites utilized various ESTs to treat animal waste while two sites maintained a conventional waste treatment technology. Each farm was sampled during one warm and one cool season. Each site and related waste treatment technology is briefly described below:

Barham Farm is a 4,000 head farrow to wean operation located near Zebulon, North Carolina (35.70°N, 78.32°W, 130m MSL). Each hog barn contained a fan ventilation system, sometimes referred to as tunnel ventilated. This site utilized a covered in-ground ambient digester as a potential alternative waste treatment system. The in-ground ambient digester may be considered as a primary treatment lagoon (4,459 m^2) that had an impermeable polypropylene covering over its surface. All the emitted gases including methane and other organic gases were collected under the cover and periodically extracted and delivered to a generator system where the gases were converted to electricity. The effluents from the hog barns were initially directed to the primary lagoon with the impermeable cover and the effluent then flowed through a single outlet pipe into a secondary storage lagoon (19,398 m^2). Here, the liquid waste was treated via a de-nitrification/biofiltration process. The treated wastewater was then used for two purposes: to flush fresh effluent from the hog barns and as a spray over agricultural crops for nutrient enrichment purposes (Cheng et al., 2000).

Grinnells Laboratories is located on the North Carolina State University campus in Raleigh, NC (35.47°N, 78.40°W, 107 m MSL). It should be taken into account that this site was located in a non-rural area. This site utilized a Ganet-Fleming Belt System that consisted of the retrofit installation of a conveyor belt type apparatus in the swine production facility to convey the manure wastes generated therein. The process separated the liquid wastes and the solid wastes as they were deposited inside the production facility. The solids were then managed through a gasification process, which involves the burning of a substance in a low-oxygen environment to convert complex organic compounds to gases. The gases were collected and used to make fuel-grade ethanol. The liquids received further treatment via a sequencing batch reactor. There is no storage lagoon located at this site (Koger et al., 2000).

Howard Farm, located near Richlands, NC (34.84°N, 77.50°W, 5 m MSL), utilized a "Solids separation/Constructed Wetlands" system as its potential waste treatment system. Effluents from the hog barns were directed initially to a solid separator where the solid waste was separated from the liquid waste. The solids were then removed to an off-site facility and liquid waste was put into two outer lagoon cells (outer cell 19,366 m^2; inner cell 10,256.3 m^2). As the wastewater traveled around the cells, it encountered the constructed wetlands, which treated the wastewater effluent through microbial utilization and the root substrate of the wetland plant species. The treated wastewater was then filtered into a finishing lagoon (7,428 m^2) where it was used in a manner similar to Barham Farm, i.e., the wastewater was recycled to flush more effluent through the hog barns and as a spray for agricultural crops. Containment houses located on the property utilized a fan ventilation system (Humenic, 2000).

Stokes Farm and Moore Brothers Farm operate a conventional (i.e., lagoon and spray) technology as the primary means of handling effluent. This method of waste treatment is the same type that is currently used by most farms in North Carolina. Effluents flow from the hog barns into an on-site storage lagoon. This wastewater is then used to flush effluent from the houses and as spray over agricultural crops. Stokes Farm is located near Greenville, NC (35.43°N, 77.48°W, 17 m MSL). The storage lagoon is 15,170 m^2 and the hog barns utilize a natural ventilation system. Moore Brothers Farm is located in Jones County near

Kinston, NC (35.14°N, 77.47°W, 13 m MSL). The storage lagoon is 30,630 m^2 and the confinement houses on site employ fan ventilation.

Sample Collection and Sampling Strategies

Ambient air samples were collected in 6-Liter electropolished stainless steel SUMMA canisters, evacuated to a sub-ambient pressure of <0.05 mm Hg. During sample collection, the valve on the canister was opened slowly over a timeframe of ~4 minutes and then fully opened on the order of 1 minute, thus allowing for a ~5 minute point sample to be collected.

Samples were collected during the 12:00-13:00 Eastern Standard Time (EST) period at various suspected source areas including lagoons, barn ventilation fans, and at "strong" odorous areas, determined through sense of smell, for each particular site. Simultaneous samples were collected at upwind and downwind locations on the farms in an effort to determine VOCs originating from the farm.

VOC Sample Analysis

The canister samples were taken to the National Exposure and Research Laboratory (NERL) of the US Environmental Protection Agency (EPA) located in the Research Triangle Park, NC, where they were analyzed using gas chromatographic (GC) procedures. All samples were analyzed by GC flame ionization detection (FID) combined with a cryogenic preconcentration approach. The GC column was a 60m x 0.32mm ID fused silica column with a 1μm liquid phase thickness (J & W Scientific, Folsom, CA). The GC column was temperature programmed and consisted of a -50°C initial temperature for two minutes followed by temperature programming to 200°C at a rate of 8°C/minute. After a 7.75 minute hold period, the column temperature is programmed to 225°C at 25°C/minute rate and held at that temperature for 8 minutes. This temperature programming sequence provided separation of the C_2-C_{12} compounds and conditioned the column for proceeding samples. Liquid nitrogen is used as the cryogen to obtain sub-ambient temperatures.

The GC/FID system was calibrated using 0.25 ppm propane in air NIST SRM (National Institute of Standards and Technology Standard Reference Material). Compound identification was determined using a CALTABLE consisting of more than 300 VOCs with corresponding column retention times.

A gas chromatograph equipped with a mass spectra detection system (GC/MS) (Hewlett-Packard Model 6890/5972, Avondale, CA) was used to verify compound peak identification. The GC/MS system served to both verify compound identification as well as to identify unknown compound peaks. Generally, 1-2 samples collected during each sampling campaign were selected for GC/MS analysis, based on the observed high peak concentration levels and/or the occurrence of unknown peaks.

Results

Measurement campaigns for this study were conducted as the farms became steady-state with the individual technologies in place. Due to the nature of Project OPEN, the farms were available for sampling for about two week increments in each warm and cold season, resulting in some limitations of our sampling strategies. The data results presented here consist of one day sampling at each swine farm facility for both warm and cold seasons. Highest VOC concentrations were typically observed at the hog barn ventilation locations for all sites. These specific results provide the most suitable database to compare both composition and concentration differences between sites and for both seasons.

Identification of the VOCs with the GC Systems

Using a GC/FID approach, individual VOCs are identified by column retention time using a detailed CALTABLE containing known VOCs and their corresponding retention times prepared from the analysis of known VOC mixtures. At the outset of this study, the GC column retention times for many of the sulfur containing VOCs were unknown. A sample collected at the outlet of a pipe leading from the covered lagoon to the electric generator system at the Barham Farm during the April sampling period greatly assisted in the identification of many of these sulfur compounds. This pipe transported methane as well as other organic gases produced from a primary treatment lagoon fitted with an impermeable cover to a generator system that converted these gases to electricity. The GC/FID analysis results of this sample indicated a complex pattern of peaks, several of which were not in the existing CALTABLE. The sample served to demonstrate the complex VOC mixture produced by the treatment of hog waste that may be released to the ambient air. The processed sample using the established CALTABLE for GC peak identification indicated the presence of several unidentified peaks. Analysis of this canister by GC/MS provided identification to many of the unidentified compounds observed with the GC/FID analysis. Since identical GC columns and temperature programming approaches were used for both GC systems, the unidentified peaks observed on the GC/FID system were located on the GC/MS system and compound identifications were determined.

Sulfides were of particular interest because many produce distinct malodors. Seventeen sulfur-type VOCs were identified, including thiophene, 2-methylthiophene, 3-methylthiophene, methyethyldisulfide, 2-ethylthiophene, 2,5-dimethylthiophene, 3-ethylthiophene, 2,3-dimethylthiophene, methylisopropyldisulfide, methylpropyldisulfide, methyl-sec-butyldisulfide, and dimethyl tetrasulfide and eventually added to the GC/FID CALTABLE to use for the other canister samples collected at the swine farm sites. The three largest peaks observed from the GC/FID at column retention times later than isobutane were dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide. These compounds represented 21.1, 17.7, and 24.4%, respectively, of the total concentration of all the GC compound peaks eluting from the column between isobutane and the last observed GC compound peak. No neat compounds or standard mixtures were available for 100% positive identification of these compounds; however, compound molecular weight and boiling point were considered to be appropriate for observed GC column retention times. Two other sulfur-containing VOCs also observed in the GC/MS results included carbonyl sulfideand carbon disulfide. Neither compound is expected to respond in the FID and would therefore not be determined with the GC/FID results. Other VOCs identified in the sample by GC/MS included alkanes, alkenes, ketones, and aldehydes.

To evaluate storage stability, this complex sample first analyzed on May 13, 2002 was stored in the laboratory for more than a seven-month period and reanalyzed by both GC/FID and GC/MS on two separate occasions: July 11, 2002, and January 31, 2003. The sulfur-type VOCs are considered to be unstable in SUMMA canisters and quickly removed by the container surfaces. With some exceptions, the composition of the compounds remained stable upon reanalysis. Particularly, several of the sulfur-type VOCs were observed to be quite stable. Almost no change was observed for dimethyl sulfide over the 7 month period. Two other sulfur-type VOCs, i.e. dimethyl disulfide and dimethyl trisulfide, appear to undergo conversion rather than surface loss. Over the 7 month storage period the 17.7 to 32% increase in dimethyl disulfide appears to be compensated by the 24.3 to 7.3% loss of dimethyl trisulfide. Loss, or most likely conversion, of the lesser abundant dimethyl tetrasulfide also occurs during the 7 month period. The reason for the dramatic change in these compounds is unclear. The hydrocarbon-type VOCs appear to be quite stable over the storage period. Canister surface passification by water vapor in the canister is credited for storage stability.

VOCs Observed at Hog Barns

Highest VOC concentrations generally observed at each of the five swine facilities were sampled at the barn ventilation locations. With the exception of Stokes, this location was directly in front of the fan ventilation systems. At the Stokes site, natural open-air barn ventilations are utilized rather than ventilation fans and samples collected next to or between the barns were selected for comparison. To better evaluate the VOCs coming from the barns, corresponding background (i.e., upwind) samples were simultaneously collected when the barn ventilation fans were sampled.

It is expected that the observed VOC composition at the ventilation outputs consists of background ambient air combined with VOC sources within the barn facility. Ideally, activities within the hog barns at each of the different site locations are expected to be uniform; however, it should be noted that the number of animals as well as the animal weights, size, and type (i.e., farrowing or finish) vary from barn to barn as well as farm to farm and could affect observed VOCs measured.

Figure 1 depicts the percent contribution of the various characteristic types of identified VOCs observed at the hog barns. Percentage values were determined by summing the individual VOCs into the various compound types and ratioing these groups to total identified VOC. Oxygenated VOCs appear to be the most abundant compounds observed near the barns. Similarities are observed in terms of specie composition near the various barns at the different sites; however, concentration levels tended to vary quite a bit, although all were within the same order of magnitude. Acetaldehyde, methanol, ethanol, and acetone were among the most dominant compounds measured near the barns. These four compounds, in addition to other oxygenated VOCs measured at the various sites, generally represented ~47-73% of net total measured VOCs that were emitted from the hog barns at EST facilities. Grinnells in November and Howard in June had the highest contribution of oxygenated VOCs, ~73%. At the conventional sites, oxygenated VOCs comprised ~37-59% of net total measured VOCs. Many of these samples were analyzed by GC/MS to confirm compound identification.

Net acetaldehyde concentration, at Barham, during both sampling periods in April and November, were 16.23 ppbC and 40.12 ppbC, respectively. At Grinnells in November the net acetaldehyde concentration was determined to be 9.57 ppbC; however, acetaldehyde was not observed at a higher concentration level at the ventilation exhaust than the background sample in April. At the EST sites, ethanol was a dominant compound among all measured VOCs at all farms with the exception of Grinnells in April. Ethanol net concentration levels at Barham were 47.09 and 155.41 ppbC representing 16.6 and 40.1% of net total measured VOCs originating in the barn), in April and November, respectively. At Grinnells, ethanol net concentration was 110.74 ppbC in November (31.5% of net total measured VOCs), and 43.95 and 82.75 ppbC net concentrations at Howard in June and December, (58.8% and 38.5% of net total measured VOCs), respectively. Ethanol concentrations at the two farms utilizing conventional waste treatment methods were comparable, e.g., at Stokes in September (67.65 ppbC net concentration and 28.7% of net total measured VOCs), and at Moore in February (18.7 ppbC net concentration and 22.8% of net total measured VOCs). Ethanol was not observed as a dominant compound at Moore in October. Considering the seasonal variability of these observations, temperature does not appear to be the primary or only determining factor in the concentration levels in these sample locations. High levels of methanol concentrations were observed at several sites. At Barham, during both April and November sampling episodes, the observed methanol concentration of 42.9 ppbC and 26.1 ppbC represented 15.1 and 6.8%, respectively, of net total measured VOCs originating in the barn. At Grinnells in April, methanol concentrations were measured at 23.3 ppbC (20.2% of net total measured VOCs originating in the barn). Acetone was a dominant compound in the hog barns at all farms with the exceptions of the EST sites, Howard and Barham in June and November, respectively. At all sites where comparisons were made, acetone contributed ~3-12% of the net difference for total measured VOCs.

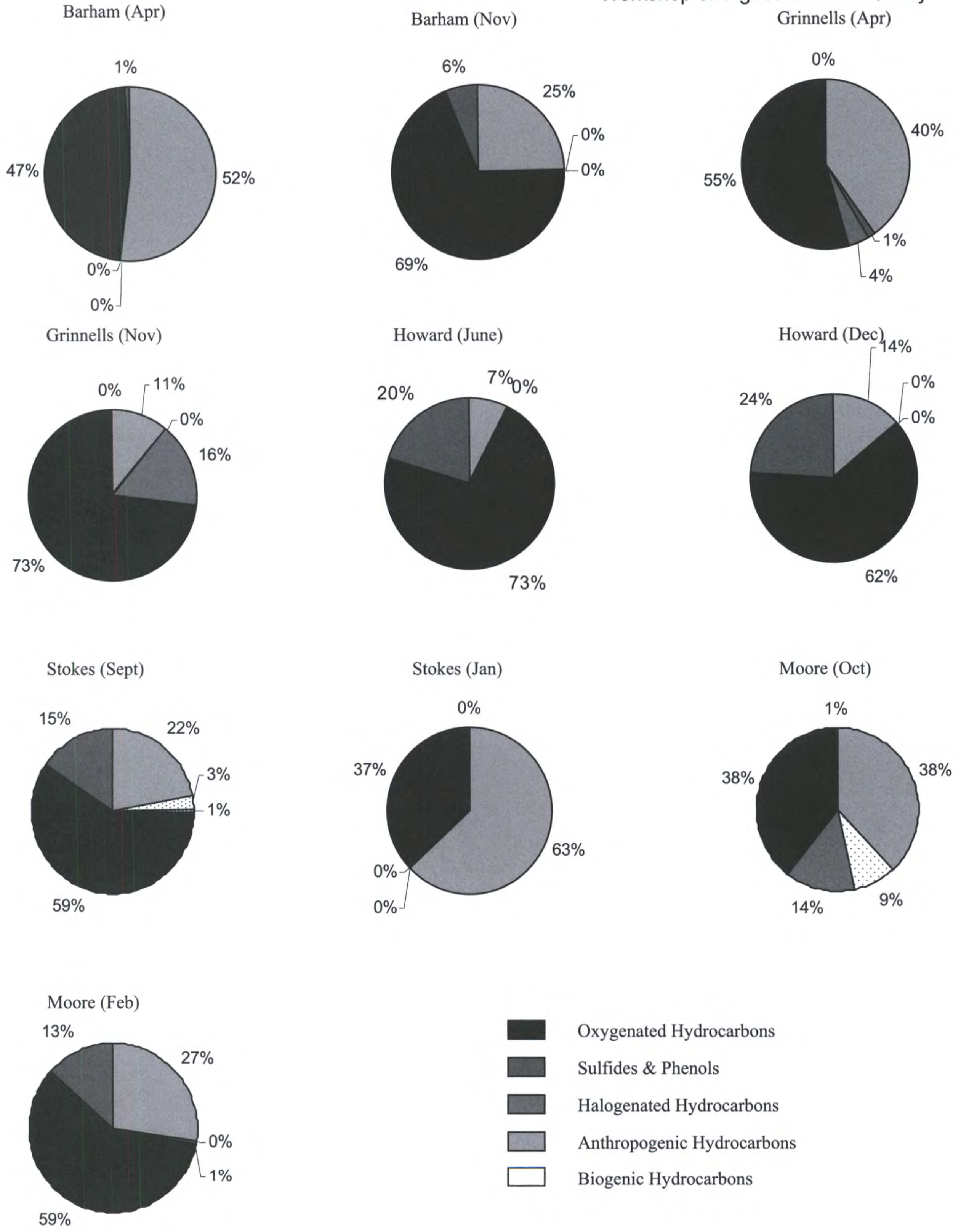

Figure 1. Total percent contributions of various types of dominant VOCs observed within ~1 meter of hog barn ventilation systems at each of the sampling sites. Sampling for each site was conducted during one warm and one cold season

Detected Sulfur and Phenolic Compounds

Dimethyl sulfide and dimethyl disulfide were the two sulfur-type VOCs frequently observed at all of the site locations that were verified by GC/MS and quantified by GC/FID. These compounds are recognized as malodorous VOCs with odor thresholds, defined as the concentration at which odor is first detected, of 2.24 and 12.3 ppb, respectively (Schiffman et al., 2001a). Dimethyl sulfide was measured at levels above its odor threshold at Barham in November, (14.4 ppbC net total concentration) and at Howard in December (6.6 ppbC net total concentration). At the barn ventilation systems for all sites, dimethyl sulfide was measured above the respective background levels with the exception of Stokes Farm in January. In this instance, the levels were comparable, 0.21 ppbC measured at the barns and 0.25 ppbC upwind. For all sites, dimethyl sulfide was detected in the background ambient air with the exceptions of Grinnells in April. At the barn ventilation systems, dimethyl disulfide was detected at the EST sites Barham, Grinnells, and Howard, during both sampling episodes. For the conventional sites, dimethyl disulfide was detected at Moore during both sampling episodes and at Stokes in September. Highest concentration levels were measured at Howard Farm, 0.77 ppbC and 2.15 ppbC, in June and December, respectively. Dimethyl disulfide was not measured (i.e., below detectable limits) in the upwind samples during any of the sampling episodes at the conventional sites. Dimethyl disulfide was measured at ≤ 0.12 ppbC at Barham in April, Grinnells in November, and Howard in June, and was below detectable limits for the other sampling episodes at the EST sites. Observed concentration levels for dimethyl disulfide at all sites never approached the 12.3 ppb odor threshold level. Figure 2 provides a comparison of the concentrations of these reduced organic sulfur compounds emitted from houses with their average concentrations in the ambient air around swine facilities. Another malodorous compound associated with swine farms, 4-methylphenol, which has an odor threshold of 5.3 ppb (Van Gemert and Nettenbreijer , 1978), was measured at the barns at the EST sites, Barham, Grinnells, and Howard during each sampling campaign. Highest concentrations of 4-methylphenol were measured at Howard in June and December, 12.5 ppbC net concentration (16.7% of net total VOCs) and 43.3 ppbC net concentration (20.1% of net total VOCs), respectively, at Stokes in September (32.7 ppbC net concentration, 13.9% of net total VOCs) and at Moore in February (10.50 ppbC and 12.8% of net total VOCs). 4-methylphenol was not detected at Stokes at all during the January sampling period or at Moore in October. To convert the measured ppbC concentrations of 4-methylphenol to ppb, an ECN value of 6.38 was used (Jorgenson et al., 1990). Only the December measurement at Howard, i.e., 43.3 ppbC/6.38 or 6.78 ppb, exceeded the compound odor threshold of 5.3 ppb.

We note that carbonyl sulfide and carbon disulfide were detected through GC/MS analyses but could not be determined by the GC/FID. Known standards of these compounds were not available to obtain quantitative results with the GC/MS system. Carbon disulfide has an odor threshold of ~16 ppb and there is no known odor threshold established for carbonyl sulfide (USDHHS, 1993). Schiffman *et al.* (2001b) determined that intensity of the odorous emissions from swine facilities resulted from the combined effect of odorous compounds present at sub-threshold concentrations in addition to individual compounds observed above their respective odor threshold levels.

The reduced organic sulfur compounds observed at the exhaust ventilation fans of each farm were normalized by live animal weight (LAW) in the barn (ppbC/1000kg). These results are presented in Figure 3. It is important to keep in mind that the age and type of animal, in addition to LAW, varied from farm to farm. At Barham, concentration levels were 0.021 ppbC/1000kg and 0.046 ppbC/1000kg in April and November, respectively. At Grinnells total levels were 0.079 ppbC/1000kg in April and 0.411 ppbC/1000kg in November. At Howard sulfur concentrations were 0.068 ppbC/1000kg in June and 0.141 ppbC/1000kg in December. Grinnells had the overall highest normalized concentration during the November sampling period. The lowest normalized levels of dimethyl sulfide and dimethyl disulfide were observed at Moore where concentrations were 0.007 ppbC/1000kg in both October and February. Normalized concentration levels for these sulfur-type VOCs were consistently higher during the colder season than the warmer season at each of the farms (Figure 3) with the exception of Moore, where the normalized concentration levels were the same.

Many of the other sulfur-type VOCs were observed to have very small percent concentrations. These compounds may be present but concentration levels are below detectable limits. It is unlikely that the percent compositions of the detected compounds remained the same after emission into the ambient air.

This is due to dispersion, vertical mixing, and/or photochemical reactions that occur in the atmosphere near ground level.

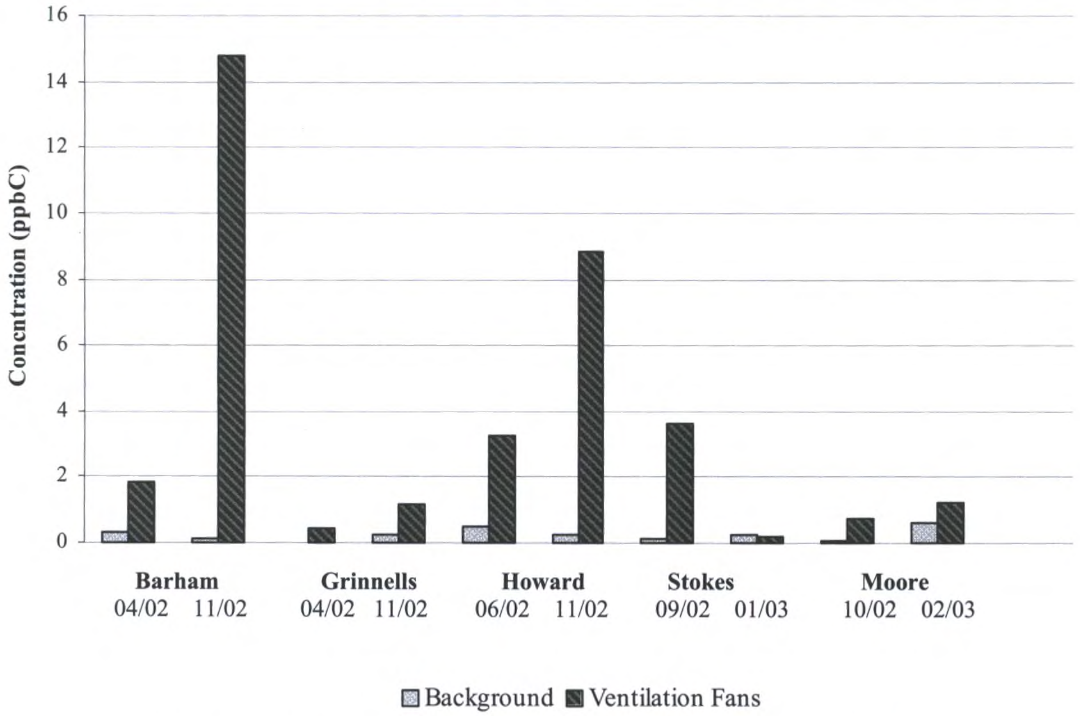

Figure 2: Total reduced organic sulfur (dimethyl sulfide and dimethyl disulfide) concentrations (ppbC) at various swine facilities in Eastern North Carolina

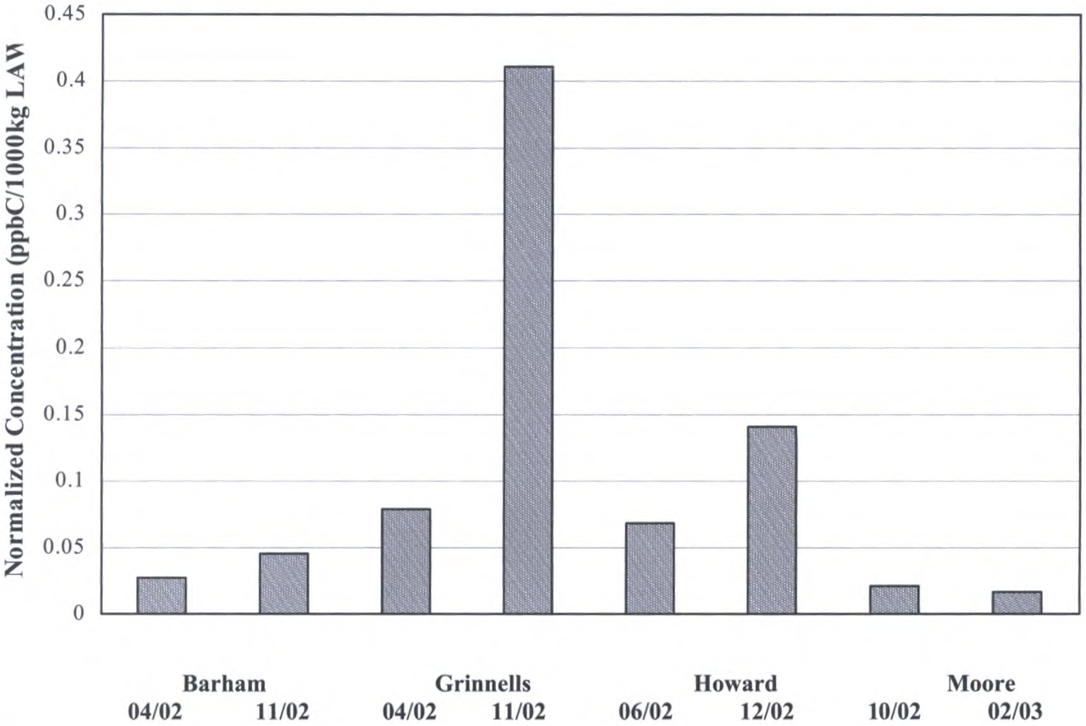

Figure 3: Total reduced organic sulfur concentrations (dimethyl sulfide and dimethyl disulfide) (ppbC) detected at ventilation fans, normalized by live animal weight (LAW)

Conclusions

A total of 110 samples were collected by means of SUMMA electropolished stainless steel canisters to characterize volatile organic compounds (VOCs) detected at five swine facilities in Eastern North Carolina between April 2002 and March 2003. Two sites employed traditional lagoon and field spray technologies; while three sites utilized various potential ESTs in an effort to reduce ammonia and VOCs emissions, odor and odorants, and pathogens at swine farms. More than 100 compounds, including various paraffins, aromatics, olefins, ethers, monoterpenes, alcohols, aldehydes, ketones, halogenated hydrocarbons, phenols, and sulfides were identified and quantified by GC/FID analysis. Many of these compounds have been determined to play an important role as precursors to tropospheric ozone, fine particulate matter (PM_{fine}), and other atmospheric photochemical oxidation formation such as peroxyacetal nitrate (PAN) (Kang et al., 2001). Other compounds observed (e.g., reduced organic sulfur compounds) are related to odor and irritation senses (Schiffman et al., 2001b; Kuroda et al., 1996).

One complex sample collected at Barham Farm helped to characterize several sulfur-type VOCs, including dimethyl sulfide and dimethyl disulfide. Carbonyl sulfide and carbon disulfide were positively identified by GC/MS analysis but could not be quantitatively determined by GC/FID. Another compound commonly associated with malodors at swine facilities as well as general air toxicity, 4-methylphenol, was also identified in many of the GC/FID sample results and verified by GC/MS analysis. The GC/MS analysis of selected samples also served to verify and/or identify many VOCs reported here.

Overall, the highest VOC concentration levels measured at each of the sites were in close proximity to the hog barns. The dominant compounds observed near the hog barns from each sampling period were compared with background samples (i.e., upwind of lagoons and houses) collected in the same timeframe, with the difference referred to as the net concentration. The total measured VOCs at the hog barns were typically dominated by ethanol, methanol, acetaldehyde, and acetone. These compounds, in addition to other oxygenated VOCs measured at the various sites, generally represented ~47-73% of net total measured VOCs that were emitted from the hog barns at EST facilities. Grinnells in November and Howard in June had the highest contribution of oxygenated VOCs, ~73%. At the conventional sites, oxygenated VOCs comprised ~37-59% of net total measured VOCs. Several of these compounds, most particularly acetaldehyde, may participate in the photooxidant process to produce downwind photochemical ozone.

Dimethyl sulfide and dimethyl disulfide, both recognized as malodorous compounds, had concentration levels at the barns above the background concentration at every farm sampled with the only exception of Stokes in September. Dimethyl sulfide was measured at levels above its odor threshold (2.24 ppb) at Barham in November (7.2 ppbC net total concentration) and Howard in Decmeber (3.3 ppbC net total concentration). Grinnells had the overall highest normalized concentration of dimethyl sulfide and dimethyl disulfide during the November sampling period (0.411 ppbC/1000kg) while the lowest normalized levels were observed at Moore where concentrations were 0.007 ppbC/1000kg in both October and February. Normalized concentration levels for these sulfur-type VOCs were consistently higher during the colder season than the warmer season at each of the farms with the exception of Moore, where the normalized concentration levels were the same. 4-methylphenol, another odorous compound associated with swine waste was also measured at higher levels near the barns than the background levels at Barham and Grinnells in April, Howard and Stokes during each sampling campaign and at Moore in February. The largest net concentrations of 4-methylphenol were measured at Howard Farm in June and December, at 12.47 ppbC and 43.41 ppbC (16.7 and 20.2% of net total measured VOCs), respectively, and at Stokes Farm in September (32.7 ppbC net concentration, 13.9% of net total measured VOCs).

Acknowledgements

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Changes of Climate, Air Pollution and Growing Season in Correlation with Changes of Sun Activities

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Abstract

Continuous Measurements of air pollution and meteorological components in Europe within the last 30 years show strong changes between 1987 and 1991. After this event, we call it "Climate Jump II", SO2-based winter smog-alert-systems were cancelled and Ozone-based summer smog-alert-systems were introduced. These changes were caused by a sudden increase of temperature combined with an increase of global radiation. Both were caused by reduction of clouds initiated by a reduction of cosmic rays (neutrons) within the 22nd sunspot period: Sun observations of NASA show a stronger increase of eruptions of protons producing stronger solar winds, which were reducing cosmic radiation by magnetic deflections during this and the following period. The Climate Jump with increasing ground near temperature of about 1.2 °C in Central Europe seems to be sun made. Moreover the North Atlantic Oscillation (NAO) shows correlation with neutron flux. This leads to the assumption, that there is a causal connection between sunspot controlled cosmic rays and cloudiness, which finally leads during increasing sun activities to increasing temperature and prolongation of growing seasons in Central Europe.

Keywords: Air pollution, Climate change, Global temperature, Global radiation, Cloudiness, Cosmic radiation, Sunspots, Neutron flux, 22nd Sunspot period, North Atlantic Oscillaton, Growing Season,

Introduction

The widely forested German country Rhineland-Palatine with its industrialised towns Mainz and Ludwigshafen seems to be an area representative for Central Europe. The components SO2, Particular Matter (PMx), O3 and NO2 and meteorological components there are measured by the telemetrical controlled system ZIMEN with 31 measuring stations in forested regions and towns (ZIMEN, 2005). By Comparing trends in air pollutants and meteorological parameters one can see remarkable coincidental changes of all components between 1987 and 1991: The concentrations of SO2 and Particle Matter (PMx) decreased by more than 30 %, while Ozone concentrations, temperature and global radiation increased significant within this short time interval of only 4 years (Fig.1). As a consequence winter smog-alert systems (introduced in 1985 and concerning SO2, PMx, NO2 and CO) were cancelled and summertime smog-alert systems concerning O3 were introduced. The strong decrease of SO2 and PMx was seen mainly as a result of successful legal management to reduce emission. The strong increase of anthropogenic O3-concentrations was seen as a result of the increase in traffic (Borchert, H., 1998).

But these strong changes of pollutants since 1987 were accompanied by very strong increase of air temperature and of intensity and duration of sunshine, caused by reduction of cloud cover. It was supposed that these sudden changes of anthropogenic air pollution in this short time interval came from meteorological changes, which were combined with climate change in Europe caused by extraterrestrial influences (Borchert H., 2004).

In the following there are shown the causes of this opinion and further data to prove and stable this opinion.

Change of Temperature and Air Pollutants

The simplest method to describe climate is to study temperature.

During wintertime the monthly averages of temperature before 1987 were relatively cold (lower than 0°C, Fig. 2). The concentrations of SO2 were high. The main part of SO2 came during this time from power plants of the eastern COMECON countries, transported by cold and dry north eastern winds beneath inversion layers of about 800 m height. In wintertime 1988/89 these cold eastern winds vanished and the measured concentrations of SO2 and dust in western Germany decreased very strong, while the emissions in the eastern countries remained unchanged. Only after 1991 emissions also stopped by collapse of the emitting industries in the eastern countries and by legal reductions of emissions of power plants.

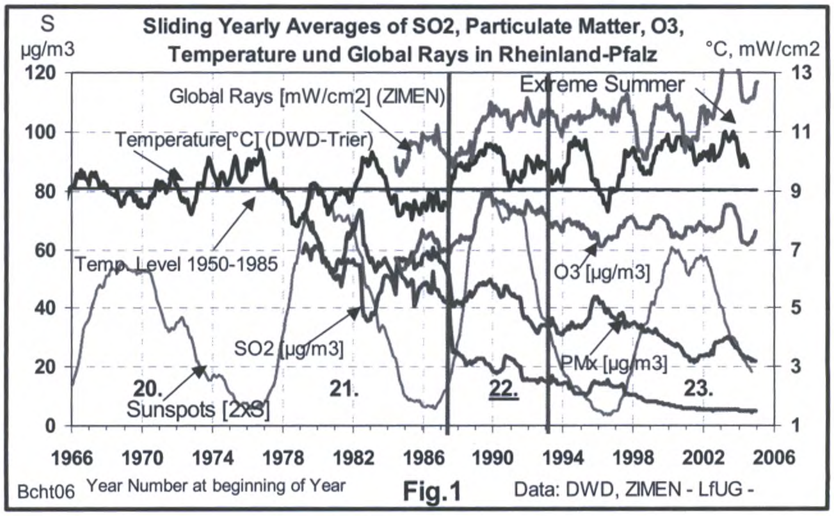


Fig.1

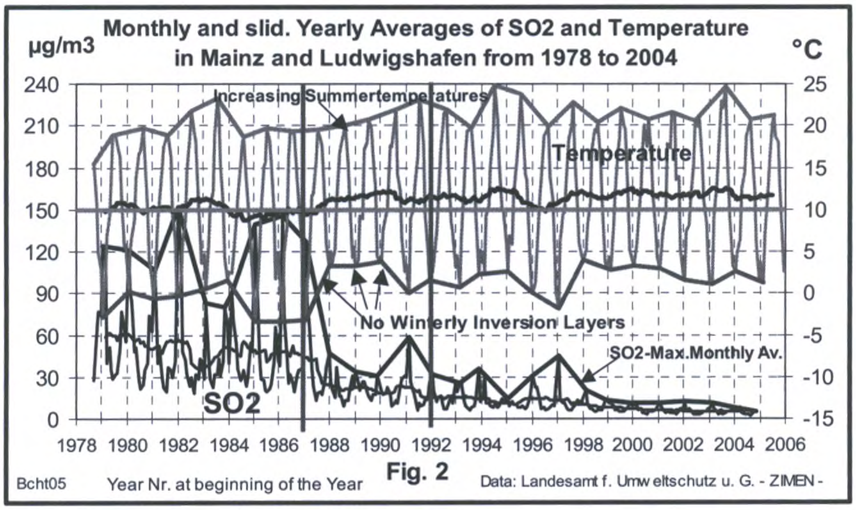


Fig. 2

Since 1989 the coldest monthly averages of temperature in wintertime are about 2 °C higher than before.

The Trend of the warmest summer temperatures increased from 1988 to 1991 by about 3 °C. After this jump of the temperature the trend of the warmest monthly temperatures was almost until now.

The trend of the sliding yearly averages of the temperature increased between 1988 and 1991 about 1.2 degrees Celsius and remains in this higher value until now.

Sliding yearly averages of NO2 in the industrialised towns Mainz and Ludwigshafen show the typical development of mainly traffic-induced immissions in western Germany (Fig3). NO2 increased in the early eighties very strongly and reached in 1984 nearly the legal limit value of 80 µg/m3 (annual mean) in these towns. With the introduction of more efficient motors and legal emission control of vehicles and of industry the immissions of NO2 decreased since 1984

But with increasing temperature since 1988 NO2 goes up again and we observe a new maximum in 1990 during this warm period. After this since about 1992 NO2 shows a continuous reduction, caused mainly by the introduction of the catalyst.

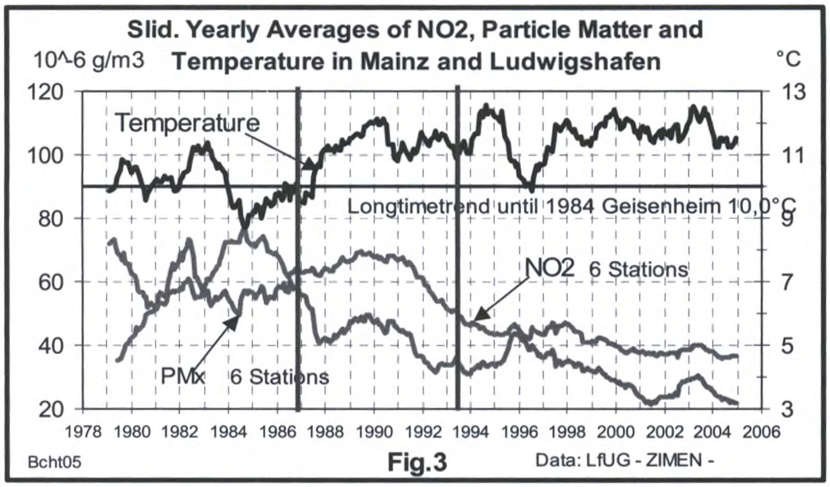


Fig.3

PMx - concentrations showed a similar behaviour to SO2 until 1988. From 1987 to 1988 PMx decreased as a result of the above-mentioned disappearance of pollution transports from eastern regions. From 1988 to 1990 PMx increased again, but now parallel with NO2. This phenomenon points to traffic as a common source of both components. Up to 1988 PMx was mainly caused by industry and power plants, after this till now it seems to be more caused by traffic. The actual PMx-level is less than a third of the level of 1987. Now it is regarded as more dangerous for human health than former knowledge believed – especially its finer parts. The new legal PM10-limits of the European Union are sometimes exceeded in towns.

Jump of Temperature in Central Europe

As ZIMEN started in 1978, we had to look for longer time measurements of meteorological components to study transport phenomena of air pollution over the landscape. To find alternations in relation to earlier times, we studied the data measured by the Deutsche Wetterdienst (www.dwd.de) at about 40 measuring points all over Germany, partly since 1900. The sliding yearly averages of the published temperatures of the DWD do not show any significant increase of long time trend between about 1940 and 1986.

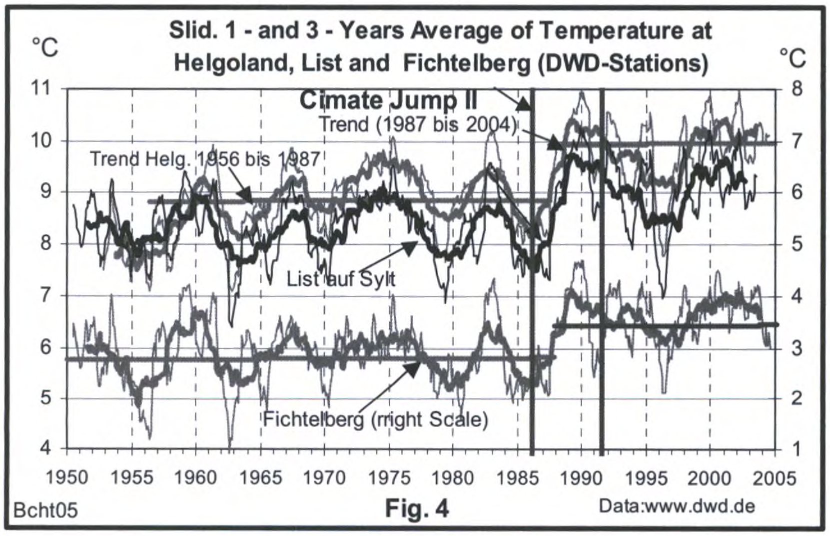


Fig. 4

The main increase in temperature in Central Europe happened between 1987 and 1990. From 1991 on until now the sliding yearly averages of the ground near temperatures oscillate around a level of approximately 0.8 °C to 1.5 °C higher than the old level. As an example Fig.4 shows the time rows of yearly averages of temperature at the islands Helgoland and Sylt in the North Sea in comparison with the Temperature at the high positioned DWD-Station of the Fichtelberg in Central Europe.

Sliding yearly averages of the temperature show an oscillation period of about three years. Therefore the sliding three years averages demonstrate the jump of temperature between 1987 and 1992 much clearly.

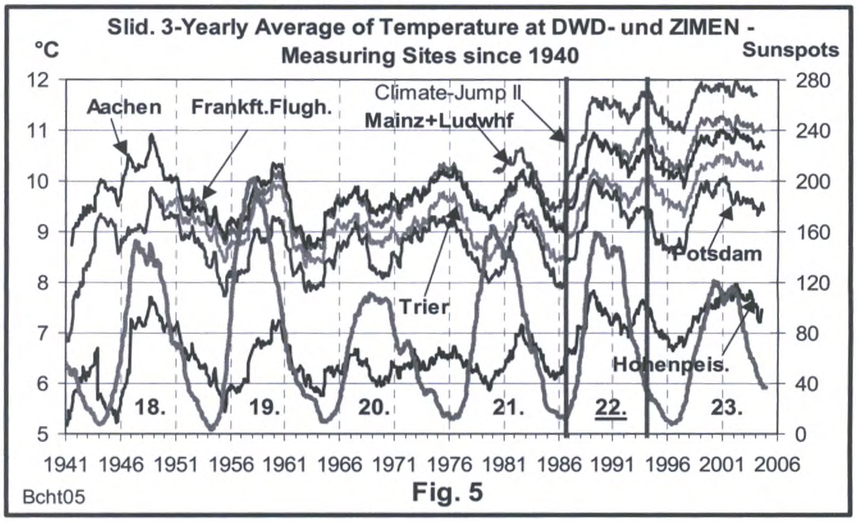


Fig. 5

Fig.5 shows the climate jump of some measuring sites in Central Europe. Absolute temperatures on mountains (Hohenpeissenberg) are lower than in valleys but all stations show the same trend. There one can find an opposite correlation between the temperature differences during the jump with the high of measuring points above NN. The curves of temperature are shown in comparison with the yearly numbers of sunspots since 1941 (Cugnon P., 2005). The jump of the temperature at all stations, called "Climate Jump II", happens with in the 22nd Sun spot period, which appeared between 1986 and 1996. During this time Earth was influenced by a lot of very strong extraterrestrial events (Thompson R., 2004), (STEDATA 22, 2003).

Tropospherical O3, Global Radiation, Sunshine and Clouds

To seek for causes of the new forest decline measurements of air pollution and meteorological components had been started since 1984 at fife forested background stations in Rhineland-Palatinate. Since this time were measured global radiation and O3. O3 is mainly produced by photolysis of the anthropogenic precursor NO2 in presence of Hydrocarbons in traffic regions and towns. It is transported into the forested regions far away from these anthropogenious precursors..

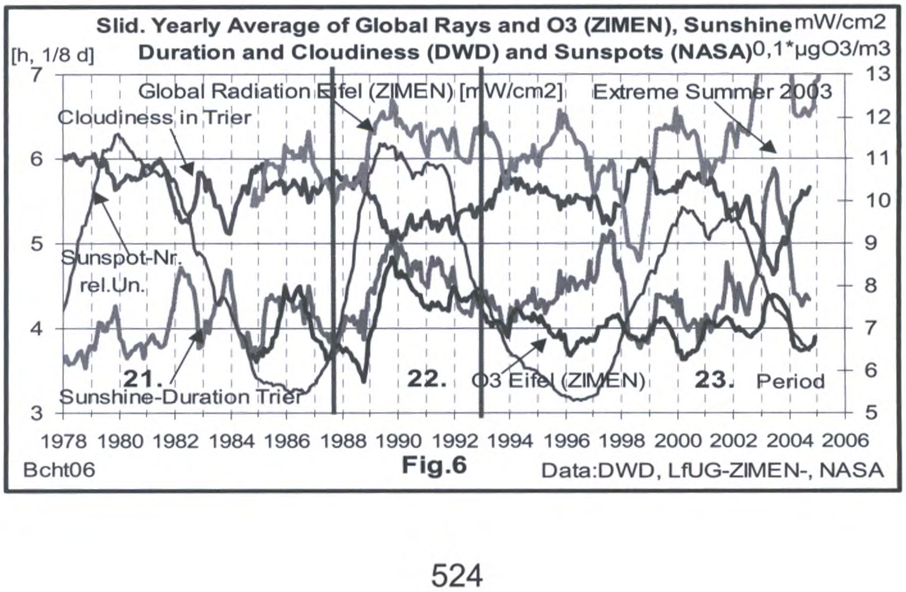


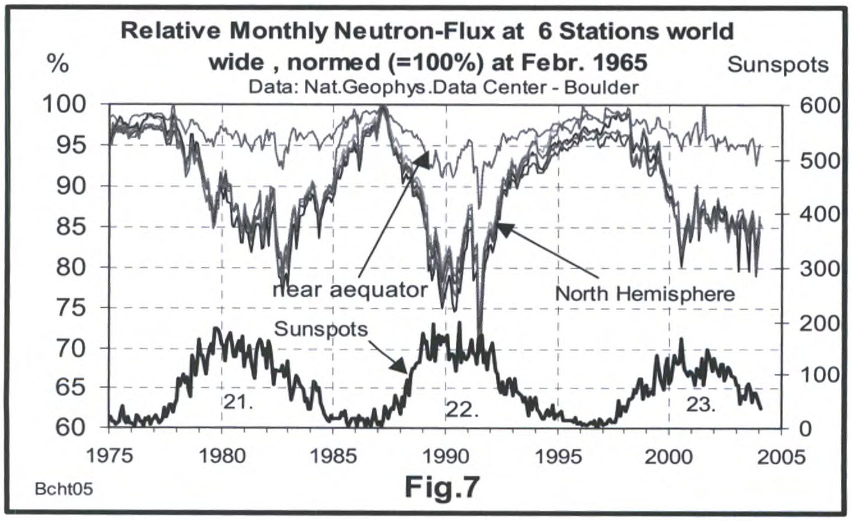
Fig.6

The strong increase of O3 in the short period between 1987 and 1990 mainly is caused by the strong increase of global radiation. After 1990 O3 was decreasing continuously as a consequence of the reduction of anthropogenic precursors by controlling the emissions of cars (ASU-controlling) and legal introduction of the controlled catalyst. Today the yearly averages of O3 are nearly constant in towns and forests at a relative low level. Yearly averages in towns are about the half of that in the forested background stations. Sliding yearly averages of sunshine duration corresponds nearly with Global Radiation (Fig.6). Naturally inverse are the time rows of cloudiness. Strong alternations of all components happen between about 1988 and 1991. The yearly averages of Global Radiation were increasing during this short time about 1.5 mW/cm3 and caused an increase of the yearly averages of temperature of about 1.2 +- 0.3 °C. The Global Radiation is strongly modulated by Cloudiness. Therefore one must look fore possible influences on Cloudiness, which steers Sunshine and in consequence anthropogenuous O3 and Temperature. These strong alternations of all components were lying in the time range of the 22nd Sunspot period with its already mentioned extreme terrestrial influences. Therefore one should seek for possible links between Sunspot frequencies and terrestrial meteorological components.

Sunspots and Neutronrates

According to a theory of Marsh and Svensmark (Eur. Org. for Nucl. Res. CERN, 2000) secondary particles of the extragalactic cosmic rays produce clouds in air saturated with water like in a **Wilson Fog Chamber** (1911). To study the production of these secondary particles of cosmic rays several physical institutes worldwide are measuring the neutron rates since 1958 (World Data Centre C2, 2005). Besides other Particles Neutrons are formed through nuclear collisions of extra galactic cosmic radiation interacting with the atmosphere. They represent the intensity of secondary particles and are relative easy to measure. A comparison with the sunspot frequencies shows, that there is a reduction of neutron flux during the maximum of each sun spot period. The frequency of Sun spots influences the intensity of cosmic rays. If the secondary particles of cosmic rays would produce clouds, than exists a link between sun activity and terrestrial climate change.

Neutron rates represent the intensity of secondary particles, which are condensation nuclei for clouds. Data collected from satellites also show that the amount of low clouds over the earth closely follows the amount of secondary particles of extra galactic cosmic radiation. Stronger solar wind during the maximum of sunspots shields the earth from extra galactic cosmic rays, therefore neutron rates are opposite correlated to the sunspot curve: Sunspots are accompanied by solar flares, which are the most energetic explosions in the solar system and have a direct effect on the earth's upper atmosphere, which becomes ionised and expands.


Relative Monthly Neutron-Flux at 6 Stations world wide , normed (=100%) at Febr. 1965

Data: Nat.Geophys.Data Center - Boulder

Fig.7

They are Roentgen Rays between 0.01 and 1 nm, reaching the Earth after 8 minutes and mark the starting point of the current of protons, which have velocities of more than 300 km/sec. The magnetic field of this "Sun wind" deflects the cosmic rays, which are high energetic protons, coming from extragalactic sources (so far as we know), and reduces the secondary particles in the lower atmosphere und on this way cloudiness. This effect depends on the number of sunspots and especially of their energetic efficiency. With this method the Sun opens its way to the earth and warms up the lower atmosphere.

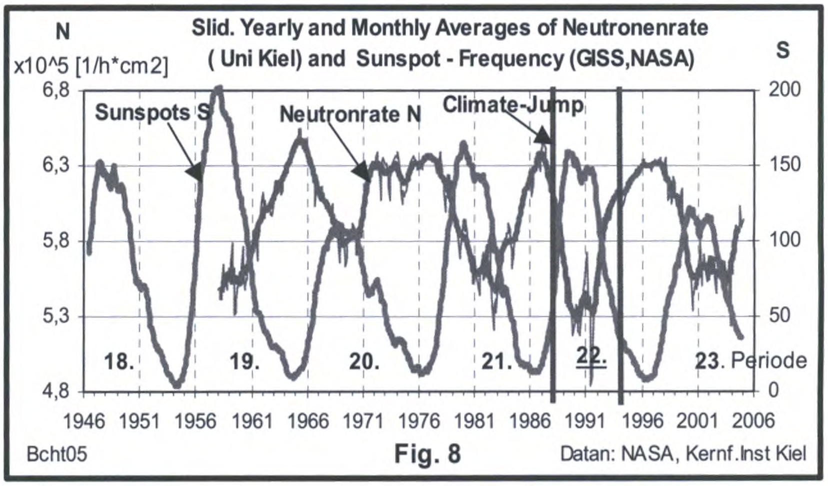


Fig. 8

This process works always und modulates the terrestrial climate. One can find harmonic correlations between the sun periods and the oscillating global temperatures (Scafetta and West, 2003). During the 22nd and actual 23rd period relative often extremely high energetic mass ejections were observed. They are to distinguish from all periods before 1986.

As a consequence of these high activities of the sun there are relative strong reductions of cosmic rays till about 30% of the monthly averages worldwide (Fig 7). Stations in the north of the 40th Latitude have nearly the same loss of cosmic rays and more than twice of equatorial places (Huancayo): Therefor it seems to be plausible that the averaged increase of global temperature is smaller in the equatorial region (0.5 to 1 Degree C/100 Years) than in the northern hemisphere (2 to 4 Degrees/100 Years) (Gray, V.R., 2003).The time rows of the Neutron rates, measured by the Institute of Physics of the University in Kiel are very good negative correlated with the time rows of the sunspot frequency (Roehrs, 2005) (Fig.8).

Neutron Rates and Cloudiness

During the 22nd Period we had a very strong reduction of cosmic rays and clouds.

A rough estimation gives, that the reduction of the Cosmic Rays of about 17 % may lead to a reduction of Cloudiness of about 13 %. During the Climate Jump this gives an increase of the averaged yearly ground near temperature of about 1.2 +- 0.3 °C in Europe.

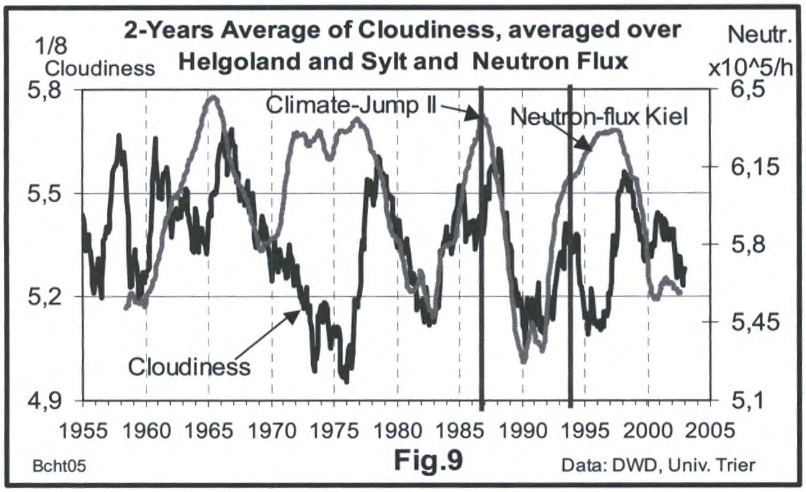


Fig.9 Data: DWD, Univ. Trier

This correlation between cloudiness and cosmic rays is the link of the controlling connection between sun activity and terrestrial climate change.

One finds this correlation at all measuring sites of the DWD, for instance at stations direct at the cost in the Northern See (Fig.9) and in the south of Germany near the Alps.

Some deviation of this rule happens between 1970 and 1978, but it seems to be a greater part of systematic delaying effect: After each main reduction of cloudiness which is correlated with reduction of cosmic rays, exists nearly systematic a delayed short time reduction of cloudiness. These "delayed reduction" seems to be caused by another meteorological influence, which is modulated by sun activity, for instance the North-Atlantic Oscillation. (NAO). Between Changes of Neutron flux, representing secondary particles of Cosmic radiation, and Changes of cloudiness seems to be a delaying time. Using a delay-time of 1 year, one gets an correlation factor of 0.8 between Neutron rates and cloudiness in Potsdam.

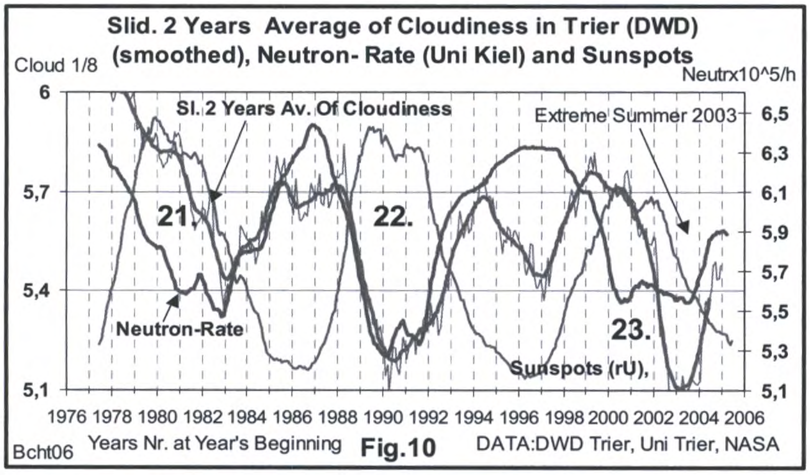
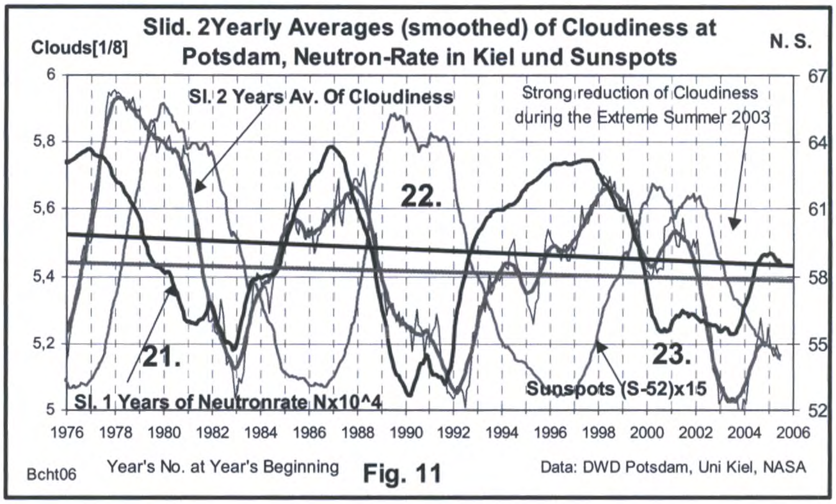


Fig.10 DATA:DWD Trier, Uni Trier, NASA

Therefore one could suppose, that cloudiness will be really influenced by drops producing cosmic rays (micro aerosols), delayed by the inertia of the oceans..

This supposition seems to be stabled by similar behaviour of the long time trends of neutron flux and cloudiness (Fig.11)



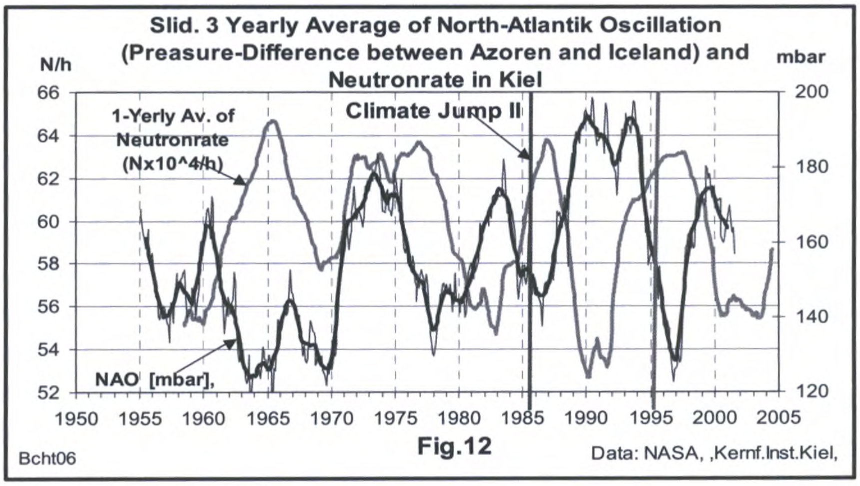
Slid. 2Yearly Averages (smoothed) of Cloudiness at Potsdam, Neutron-Rate in Kiel und Sunspots

Fig. 11

Data: DWD Potsdam, Uni Kiel, NASA

North Atlantic Oscillation (NAO) and Sun Activity

Locking for other data to support this theory one can find an relatively strong anti correlation between the time rows of the North Atlantic Oscillation (NAO) and Neutron rates especially since about 1980, when global Temperature starts to increase the second time in the last century (Climate Jump II). The NAO shows the time rows of the Difference of Air Pressure measured at Azore - Islands and at Iceland



Slid. 3 Yearly Average of North-Atlantik Oscillation (Preasure-Difference between Azoren and Iceland) and Neutronrate in Kiel

Fig.12

Data: NASA, ,Kernf.Inst.Kiel,

The opposite correlation between the NAO and Neutron rate in Fig. 12 gives rise to the opinion, that cosmic radiation influences via Swensmark- effect the NAO and by this the climate in Central Europe.

There exists a relatively strong correlation between the North - Atlantic- Oscillation and the behaviour of the weather in Central Europe, for instance the cloudiness (Fig. 13).

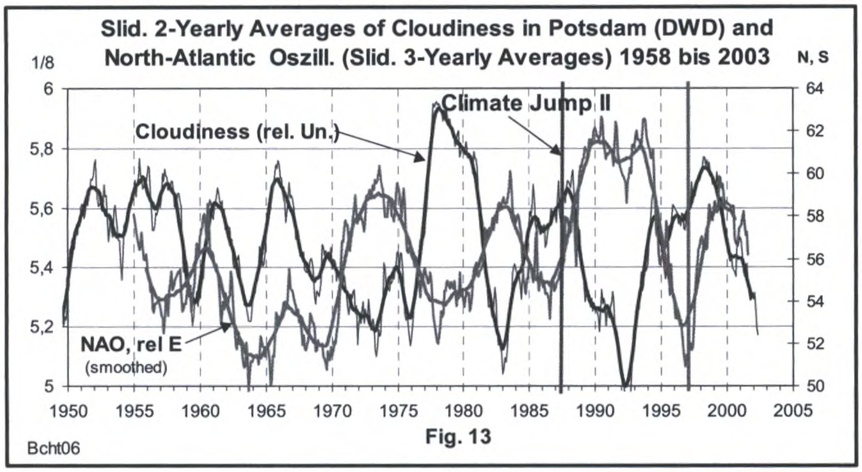


Fig. 13

Further more we can find a relative good correlation between sunspots and NAO (Fig. 14). Between the periodic changing sun activity and its influence on the earth's meteorology one can observe a certain delay-time of about one year, possibly caused by the inertia of the ocean.

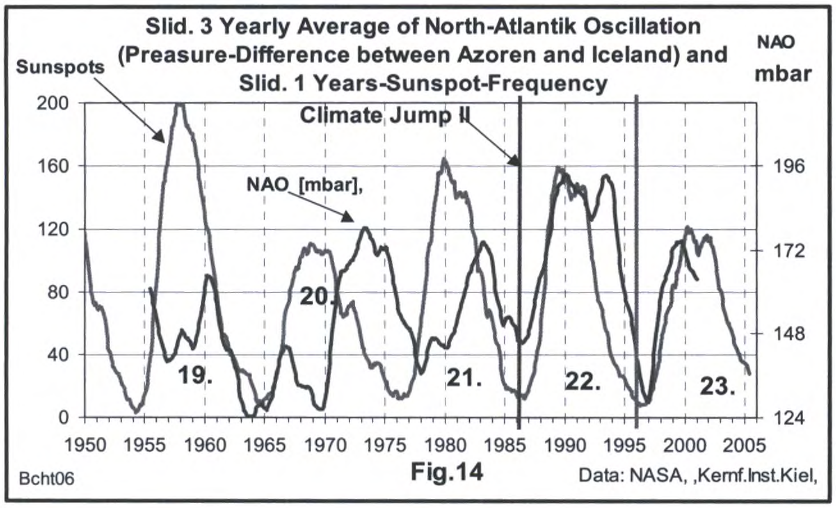


Fig.14

Data: NASA, ,Kernf.Inst.Kiel,

Cosmic Rays, Temperature and Growing Season

Time rows of temperature averaged over 4 DWD-stations in Central Germany are in wide time ranges similar to periodic alterations of Sun spot frequencies. Further they are in opposite correlation to Cosmic Radiation (Fig.15), which is good correlated with cloudiness (Fig.10). On this way there seems to be a causal chain between sun activity and development of terrestrial temperature: The strong alterations of air pollution and climate components between 1986 and 1991 seems to be a consequence of a not normal increase of sun activities with strong reducing cloudiness and increasing sun shine. During this climate jump ground level temperature increases relatively strong (about 1,2 °C +- 0,3 °C) and remains at higher long time level up to now.

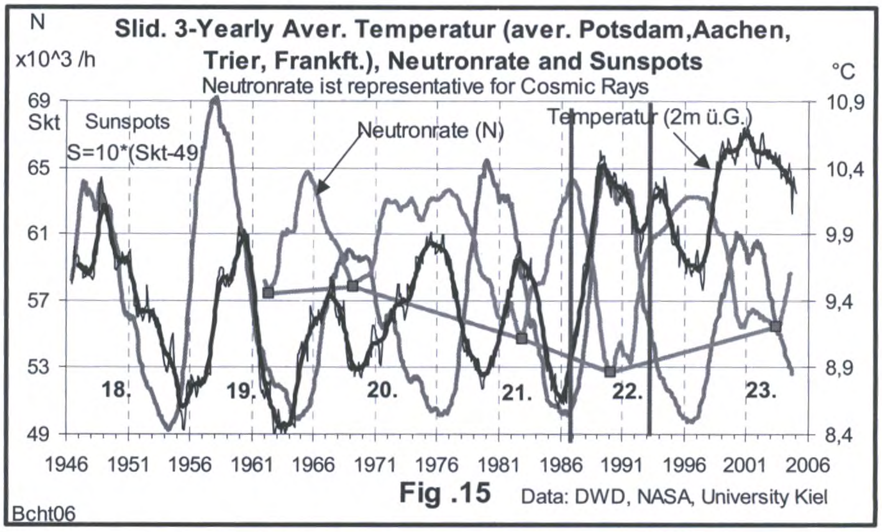


Fig .15 Data: DWD, NASA, University Kiel

As a consequence of this Climate Change at the end of the eighties one can observe a strong influence into biological systems: Fig.16 shows a correlation between the Reduction of Starting time of growing season in Central Europe and decreasing Neutron rates.

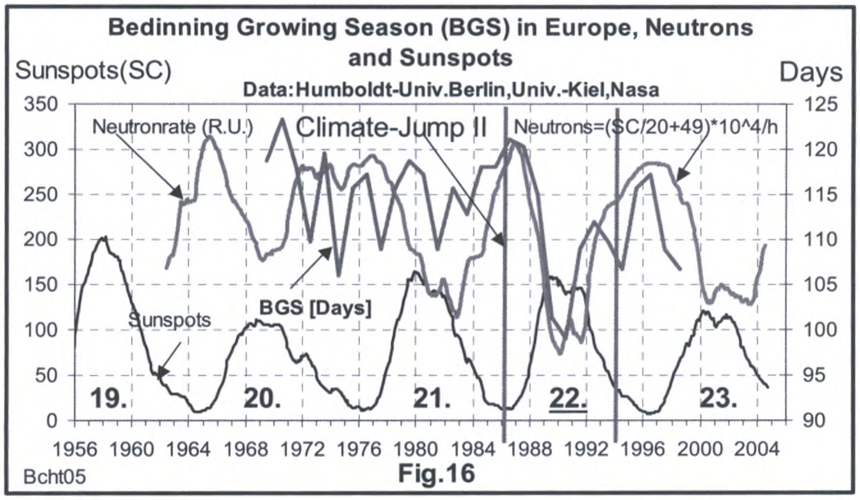


Fig.16

The prolongation of the greening time of Plants (Chmielewski, F.-M. and Rötzer, T.)

starts just with the strong reduction of Neutron Rays with beginning of the 22. Sunspot period. The Growing Season seems to be controlled by Sun activities.

Sun Emissions of Protons

To look for further observations to stable the sun made climate change during the eighties we studied by NASA published satellite measurement values. Fig 17 shows the monthly satellite-measured sums of Protons with energies higher than 10 MeV and per cm2 and sterad. These strong "Sun Winds" started during the 22nd Period 1989 with an extremely large sunspot in March and continued in October with great solar mass ejections. These proton currents produced blackouts at electric power plants in the northern hemisphere, like USA, Canada and Sweden, they disturbed wireless contacts between earth and aeroplanes and satellites, they produced auroras seen at the Equator. Such strong solar mass ejections occurred repeatedly during the 22nd and in the 23rd period until now. The NASA comments this behaviour "The Sun Goes Haywire". One of the last great sun wind events influencing earth occurred at the 15 January 2005 from a sunspot Nr. NOAA 720.

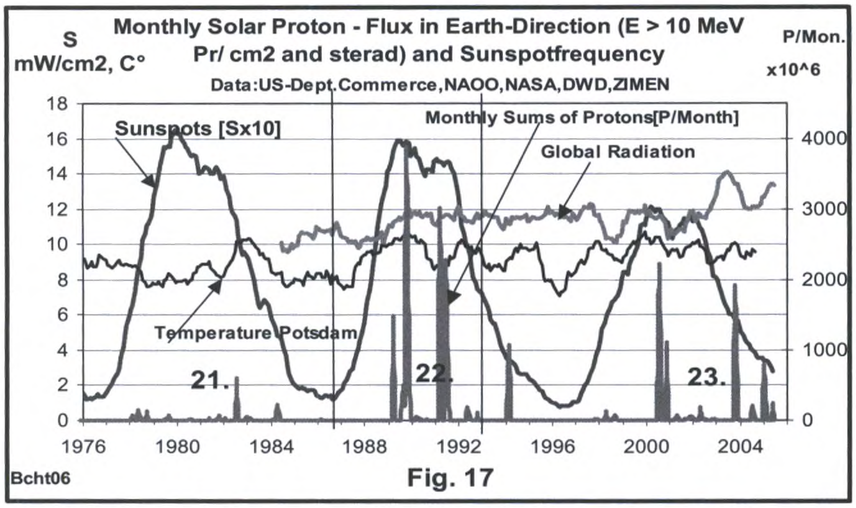


Fig. 17

This behaviour of the sun makes the fact plausible that temperature remains in tendency at a higher level than before 1988.

Global Temperature and Sunspots

This work deals with the question of the global warming: There is no continuous increase of global temperature since 1900, whereas the time rows of global temperature show two jumps since 1900: The first "Climate-Jump I" happens between approximately 1920 and 1935, the second "Climate Jump II" from 1989 to about 1994 (Fig. 14). The second is caused by special solar activities like described in this paper.

Some other observations point to extraterrestrial influences of climate change: The 11 Years averaged Sunspot periods are increasing until 1960, than they are nearly stable until now.

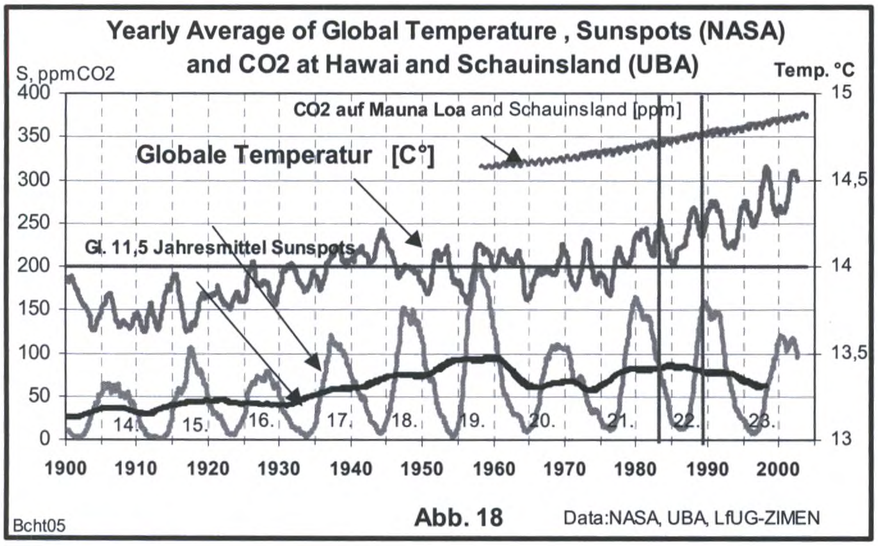


Abb. 18

The trend of global temperature increases with decreasing length of the basis of sunspot periods. The Index of the North Atlantic Oscillation (NAO) shows during Climate Jump II (1989 - 1992) a strong anomaly. The increase of CO2 is continuous and shows no jump. One can find a modulation of the increasing averages of the CO2-concentration of Hawaii by the 22nd Sun spot period. It seems to be possible, that the increasing CO2 concentration is powered by increasing sun activity too. The main cause of the sudden climate change during the eighties was the sudden increasing number of extreme height energetic mass ejections of the sun, surely caused by a special nearby constellation of the torques of the Sun and Sun System (Landscheidt Th., 2004). Further studying these phenomena with further measured data may lead also to answer the question, why the global warming seems to tend today to lag behind the increase in greenhouse gases.

Conclusion

In the last thirty years the main change of measured air pollution in Central Europe happened within the short period of 4 years between 1987 and 1991. The climate change happened during the same time interval. These events coincided with increasing sun activities, increasing intensities of sun winds and with decreasing cosmic radiation (neutron rates) with the consequences of reducing cloudiness, increasing global radiation and increasing ground near temperature. The conclusion is, that since about 1940 mainly with starting of the 22nd Sun spot period climate changed in Central Europe, which strongly influenced transportation (SO2, Dust, NO2, O3), air chemical production (O3) and concentrations of air pollution. Correlations between changes of the North Atlantic Oscillation and Cosmic Radiation point to a strong controlling influence of sun activity (Sunspot frequency and intensity of Sun Winds) to terrestrial climate change.

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Evaluation of Zeolite for Control of Odorants Emissions from Simulated Poultry Manure Storage

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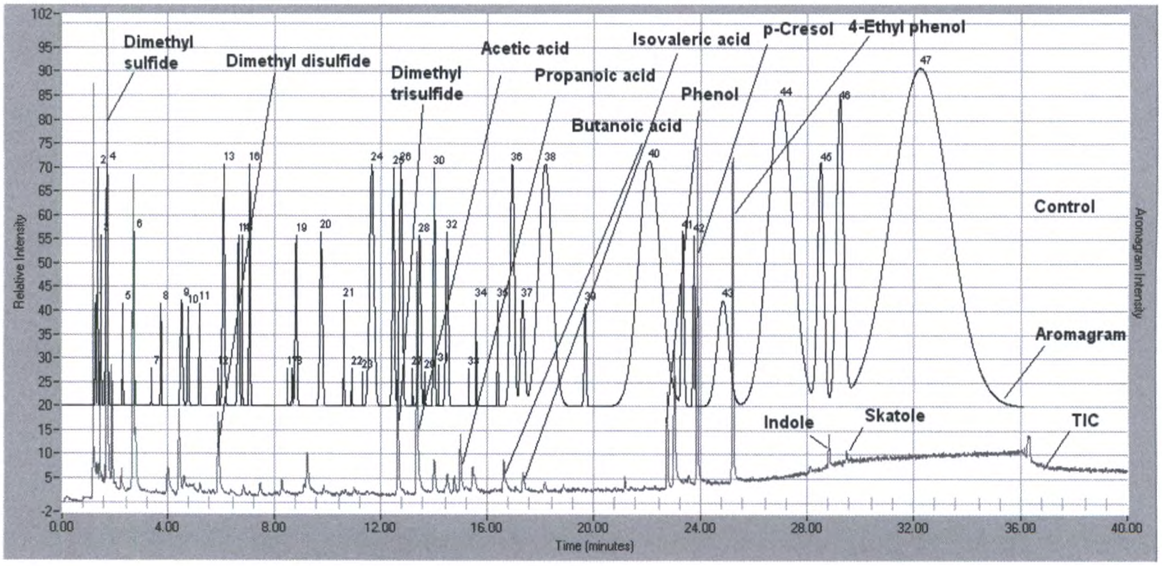
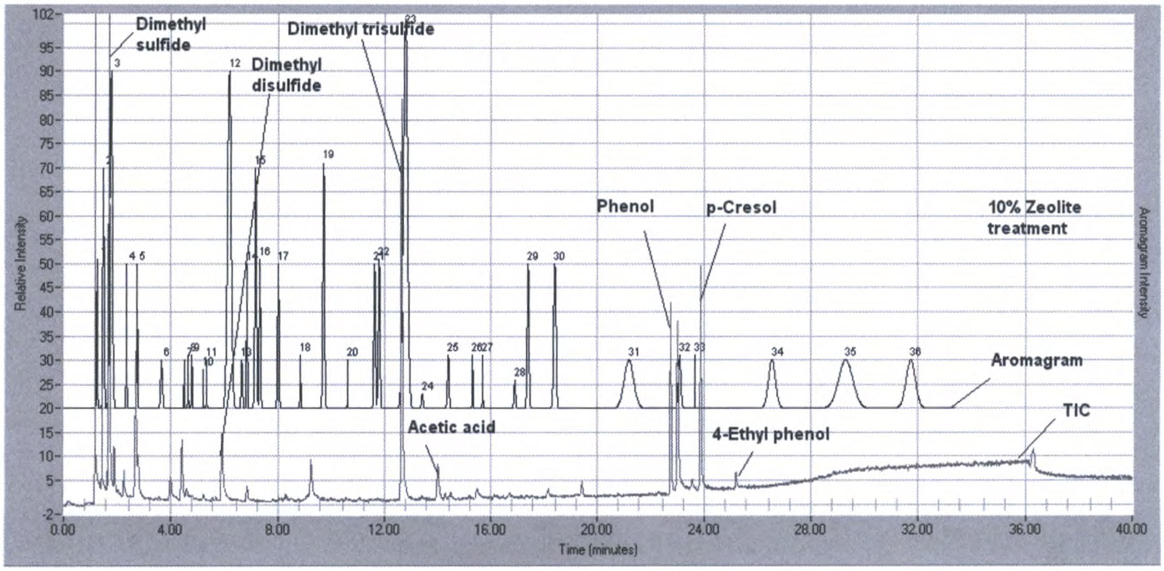
Abstract

Poultry feeding operations are associated with aerial emissions of ammonia (NH_3), volatile organic compounds (VOCs), and odor, and the magnitude of emissions is influenced by manure management practices. As a manure treatment additive, zeolites have been shown to have the potential to control NH_3. Because of their properties it is also expected that zeolites could effectively adsorb VOCs and odor. In this controlled laboratory study involving simulated poultry manure storage, the effectiveness of zeolite in controlling odor and VOCs was evaluated. In the first 2 trials zeolite was topically applied on fresh poultry manure from egg layers at the rates of 0, 2.5%, 5% or 10% (by weight). In the third trial, zeolite was applied in layers over fresh manure. Headspace samples from the emission vessels were collected with solid phase microextraction (SPME) and analyzed on a multidimensional-gas chromatograph-mass spectrometer-olfactometry (MDGC-MS-O) system for identification and prioritization of poultry manure odorants (Figure 1). Acetic acid, butanoic acid, isovaleric acid, indole and skatole were consistently controlled, with the reduction rate being proportional to the zeolite application rate. Dimethyl trisulfide and phenol were consistently generated, and with a few exceptions, the rate of generation was proportional to the application rate. Average reduction of the total odor was 67% (±12%) and 51% (±26%) for the two topical applications, respectively, while no significant reduction of VOCs and odor was found for the layered application.



Part A



Part B

Figure 1. Comparison of total ion chromatogram (TIC) (lower, red line) and aromagram (upper, black line) of VOCs emitted from poultry manure between control and 10% zeolite treatment (Part A) and control (Part B). Air samples were collected using Carboxen/PDMS 85 µm SPME fiber and 10 min sampling time. Numbers signify odor/aroma events.

Correlation of Meteorological Data to Nitrogen Mass Balance of Broiler Production as Influenced by Litter Age

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Abstract

Emission of nitrogen (ammonia) from commercial broiler facilities has become a topic of increased concern, debate and research efforts worldwide. Most studies to date have been performed in commercial facilities by measuring ammonia concentrations and ventilation rates, resulting in large variation and uncertainty in reported results. Recent studies by our laboratory have employed the mass balance technique to quantify nitrogen loss from pens of commercial broilers raised under simulated commercial conditions on recycled litter. Eighteen consecutive flocks were reared to 42 days of age with an average ending body weight of 2.2 kg. All birds and feeds were obtained from a commercial broiler integrator. Correlation coefficients were determined for nitrogen loss and meteorological data. Nitrogen loss was significantly correlated to average temperature when all flocks were considered. Correlations were further determined in sub groups of the flocks (flock 1-5 vs flocks 6-18). Nitrogen loss was not correlated with average temperature during flocks 1-5 but was significantly correlated during flocks 6-18. Thus litter age has an impact on nitrogen loss. Relative humidity was not significantly correlated to nitrogen loss. These results suggest that older litter may not result in greater ammonia loss during cooler weather. In summary, this study demonstrated that seasonality is an important factor affecting nitrogen volatilization from broiler facilities.

Introduction

The main factors that influence the volatilization of ammonia (NH_3) from poultry manure have been identified as pH, temperature, and moisture content (listed in decreasing order of importance) (Elliott and Collins, 1982). The process of NH_3 release from the breakdown of uric acid in poultry manure is catalyzed by enzymes produced by microorganisms (reviewed by Nahm, 2003), and microorganism growth and proliferation are sensitive to temperature and moisture content (water activity). As a result, the factors of temperature and moisture will greatly influence the formation of NH_3 in broiler litter under commercial conditions.

Ambient climatic conditions outside a broiler house will inevitably influence temperature and moisture conditions within the house as a result of necessary ventilation. The purpose of this report is to compare N loss data obtained from the N mass balance study presented in Coufal et al. (2006) with meteorological data corresponding to the grow-out period of each flock. In this manner, the influence of ambient temperature and moisture (humidity) on N retention in litter materials and N lost to the environment will be accessed.

Materials and Methods

Nitrogen mass balance data for 18 consecutive flocks of broilers reared on the same recycled litter was presented in Coufal et al. (2006). Easterwood Airport in College Station, Texas is located approximately 0.8 km from the Texas A&M University Poultry Research Center where the nitrogen mass balance study was performed. Meteorological data for each day during the grow-out period of each flock was obtained from the National Climatic Data Center website for College Station, TX (NCDC, 2005). Data for daily average dry bulb and dew point temperature were averaged over the 40 to 42-d grow-out period for each flock. Daily average dry bulb temperature and daily average dew point temperature were used to calculate daily average relative humidity (RH). Daily RH was then averaged for all days in each flock. Pearson correlation coefficients (r) between meteorological variables, N partitioned into litter, cake, all litter materials, and N lost to the environment were determined using the CORR procedure of SAS[1]. Correlations

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[1] SAS for Windows, Version 8.01, SAS Institute, Cary NC

were considered significant at $P<0.05$. Correlations were determined considering all 18 flocks and considering flocks 1 to 5 separate from flocks 6 to 18 to investigate the effect of litter age.

Results

Pearson correlation coefficients between meteorological data, N partitioned into litter, cake, all litter materials, and N lost to the environment considering all 18 flocks are presented in Table 1. All litter N and N loss were significantly correlated to average dry bulb and dew point temperatures. Relative humidity was not significantly correlated to any N balance variables. This can be attributed to the fact that no consistent pattern of variation among flocks was observed for RH, while N balance variables did vary among the flocks. Although no data on RH levels inside the broiler house were collected, it can be assumed that RH levels within the house will usually be elevated. This would be especially true in the hot weather conditions when the evaporative cooling system was used to cool the air entering the house. In cold weather, RH levels would also be expected to be elevated within the house as ventilation rates are reduced to retain heat in the house. Therefore, high RH would promote NH_3 formation year-round and would not be expected to contribute to the observed variations in N loss.

TABLE 1. Pearson correlation coefficients (r) between meteorological data, nitrogen partitioned into litter materials, and nitrogen lost to the environment in flocks 1 to 18[1]

	All Litter N[2]	N Loss
Ave. Temp.[3]	-0.75 (<0.001)	0.69 (0.002)
Dew Point[4]	-0.79 (<0.001)	0.73 (0.001)
Relative Humidity	-0.18 (0.483)	0.23 (0.353)

[1] Numbers in parentheses are P-values for test of significant correlation between corresponding variables

[2] All Litter N = litter N + cake N

[3] Ave. Temp. = average daily dry bulb temperature

[4] Dew Point = average daily dew point temperature

When r values were calculated for flocks 1 to 5, no significant correlations were determined between any temperature variables and N mass balance variables (Table 2). All litter N and N loss were also not significantly correlated in flocks 1 to 5. In flocks 6 to 18, strong, significant correlations were observed between all temperature variables and all litter N and N loss (Table 2). All litter N was negatively correlated with temperature while N loss was positively correlated with temperature. Therefore, as temperature increases, the amount of N inputs partitioned into the litter materials decreases. Conversely, as temperature increases, the amount of N inputs lost to the environment also increases. Such results would be expected since it has been previously shown that NH_3 volatilization increases with temperature (Elliott and Collins, 1982; Carr et al., 1990). The correlation between average daily temperature and N loss in flocks 6 to 18 was $r = 0.85$. The differences in r between the analysis for flocks 1 to 5 and 6 to 18 indicate that litter age is an important factor influencing N retention in the litter and, therefore, N loss. This fact demonstrates that with newer litter temperature has little or no influence on N loss compared to older litter. RH and N loss were not significantly correlated in any of the analyses.

The results of this analysis demonstrate that the factors of temperature and litter age can have significant impacts on N loss from broiler facilities. It can be concluded that temperature has more influence on N partitioning than moisture (humidity) since ambient RH levels did not vary by a seasonal pattern in this study and were not found to be correlated with N loss. Therefore, litter age and ambient climatic conditions (season) are important factors to consider when quantifying and estimating nitrogen emissions from broiler housing.

TABLE 2. Effect of litter age on Pearson correlation coefficients (r) between meteorological data, nitrogen partitioned into litter materials, and nitrogen lost to the environment[1]

	Flocks 1 to 5		Flocks 6 to 18	
	All Litter N[2]	N Loss	All Litter N	N Loss
Ave. Temp.[3]	-0.33 (0.591)	-0.25 (0.682)	-0.87 (<0.001)	0.85 (<0.001)
Dew Point[4]	-0.27 (0.660)	-0.32 (0.599)	-0.90 (<0.001)	0.88 (<0.001)
Relative Humidity	0.62 (0.263)	-0.79 (0.115)	-0.18 (0.550)	0.23 (0.459)

[1] Numbers in parentheses are P-values for test of significant correlation between corresponding variables

[2] All Litter N = litter N + cake N

[3] Ave. Temp. = average daily dry bulb temperature

[4] Dew Point = average daily wet bulb temperature

Acknowledgements

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Elemental Compositions of $PM_{2.5}$ in Ambient Air Downwind of Agricultural Operations in California's San Joaquin Valley

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Abstract

Fugitive dust emissions from soil are thought to constitute a large fraction of the PM_{10} and $PM_{2.5}$ inventory in California's San Joaquin Valley (SJV) and other western air basins. The major sources of these emissions are paved and unpaved roads, construction sites, windblown dust, and agricultural activities.

$PM_{2.5}$ is considered to be among the most harmful of all air pollutants. When inhaled these particles evade natural defenses of the respiratory system and lodge deep in the lungs causing serious health problems. According to Dr. M. Waalkes of the National Cancer Institute, some heavy metals have the tendency to donate electrons and to form basic oxide. Biologically, many metals are essential to living systems and are involved in a variety of cellular, physiological, and structural functions. But at high doses, many metals become toxic. The route of exposure may affect the dose and the site where the metal concentrates, and thus the observed toxic effect.

In California's San Joaquin Valley, California agricultural operations are highly complex and potentially significant sources of $PM_{2.5}$, especially during late summer and fall.

We collected $PM_{2.5}$ samples using traditional upwind-downwind ambient sampling arrays in a variety of locations in the San Joaquin Valley. We analyzed them for elemental content using Proton Induced X-Ray Emission (PIXE), Proton Elastic Scattering Analysis (PESA) and X-Ray Fluorescence (XRF) analysis

Introduction

Soil particles become resuspended into the atmosphere of California's San Joaquin Valley during agricultural operations in the fall months and by a variety of other activities, such as construction or travel on paved and unpaved roads, during much of the year. In prior studies, we have documented the relationship between the amount of $PM_{2.5}$ generated by a soil ($PM_{2.5}$ Index) and its texture as measured by the amount of sand, silt, and clay in the soil. In this study, we document the elemental composition of a variety of soil textures. For this study we collected ambient $PM_{2.5}$ samples downwind of typical agricultural operations that caused soil dust to be resuspended into the atmosphere. The operations included disking, bed formation, and land planing.

Method

All field measurements were made under actual field conditions. A combination of upwind/downwind source isolation and vertical profiling was used to quantify $PM_{2.5}$ concentrations. The aerosol mass concentrations were calculated using the gravimetric method. The elemental composition in the filters (22 elements) was determined using three analytical methods to characterize the elemental composition of the aerosol deposits on the Teflon membrane filters: PIXE (Proton Induced X-ray Emission) analyzing elements from Na to Mn, XRF (X-Ray Fluorescence) from Fe to Pb, and PESA (Proton Elastic Scattering Analysis) for hydrogen.

PIXE and PESA technique were conducted using a 4.5 MeV proton beam produced by the 76" Cyclotron at the Crocker Nuclear Laboratory at the University of California, Davis. A schematic of the PIXE/PESA system is shown in Figure 1.

The X-Ray Fluorescence system uses a General Electric grounded molybdenum anode diffraction type X-ray tube. The x-rays produced by the tube are collimated and directed onto an aerosol sample. The sample deposit absorbs the Mo X-ray energy and re-emits the energy as x-rays characteristic to the elements present on the sample. A schematic of the X-Ray Fluorescence system is shown in Figure 2.

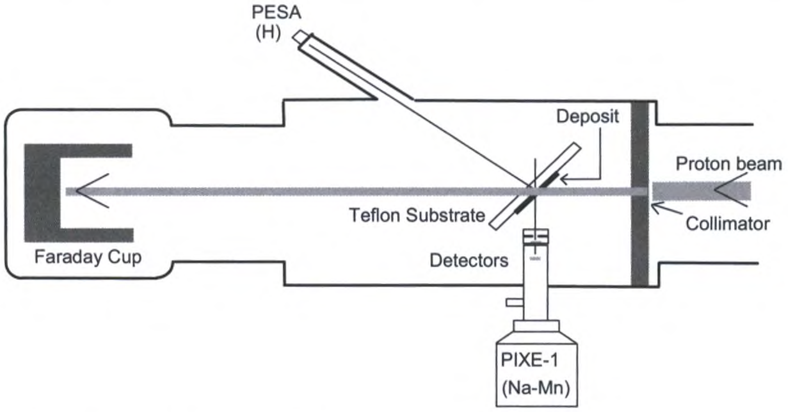


Figure 1. PIXE and PESA Filter Analysis

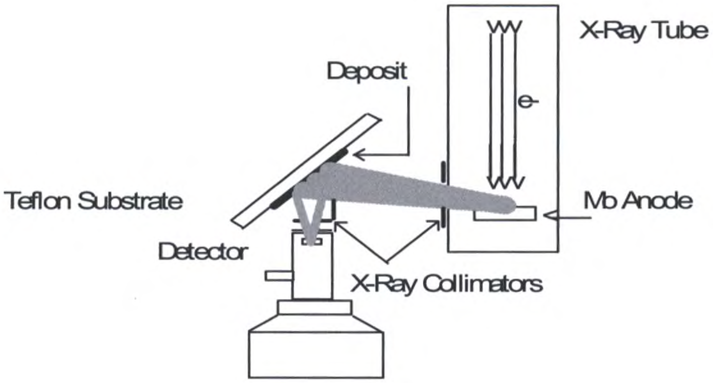


Figure 2. XRF Analysis System

Composite Variables

A soil parameter was calculated using the IMPROVE formula by adding the concentrations of five soil elements weighted by their typical oxide form in sediments as follows:

$$\mathbf{SOIL = 2.20*[Al] + 2.49*[Si] + 1.63*\ [Ca] + 2.42*\ [Fe] + 1.94*\ [Ti]}$$

The hydrogen concentration is useful as an estimate of organic mass. Sulfur was used to calculate the sulfate aerosol components which assumed to be ammonium sulfate, fallowing the IMPROVE formulas (Eldred et.al., 1987 and 1989)

$$\mathbf{Organic\ (by\ H) = 13.75 * (H - 0.25*\ [S]}$$

$$\mathbf{SO_4^{=} = 4.125 * [S]}$$

Results

The $PM_{2.5}$ mass concentrations measured for different soil textures downwind of agricultural operations varied between 31.9 and 238.7 μg/m³. Figure 3 shows the composition of the $PM_{2.5}$ collected from these samples. For all soil types examined, mineral soil accounts for 49.5% to 64.5%. Organic matter varied between 25.5% and 43.9% of the mass of all soil types, with sulfate, metals, and other elements accounting for the rest of the mass. The inset graph in Figure 3 shows the soil elements Al, Si, Ca, Fe, and Ti as a fraction of their total for the ambient samples.

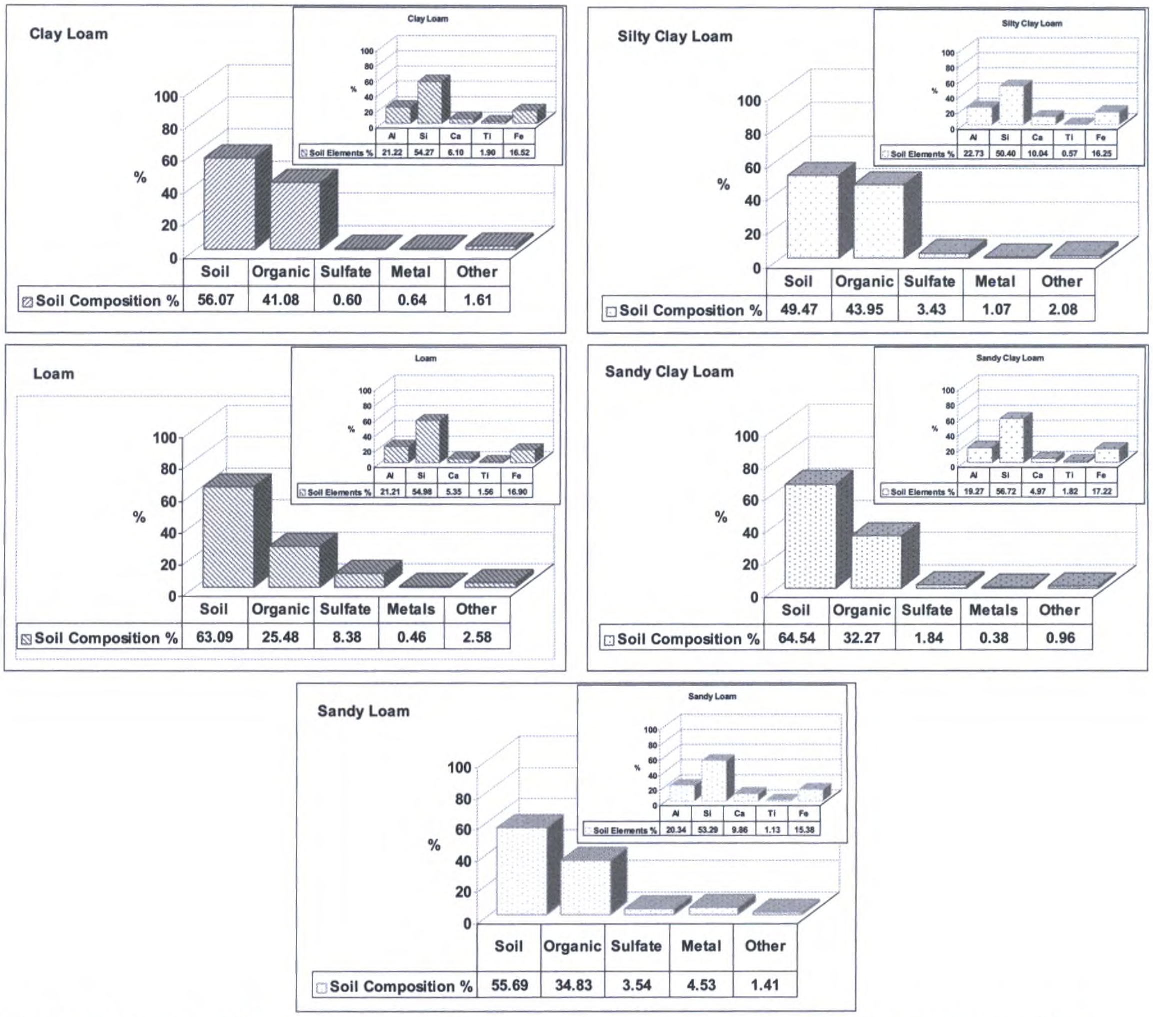
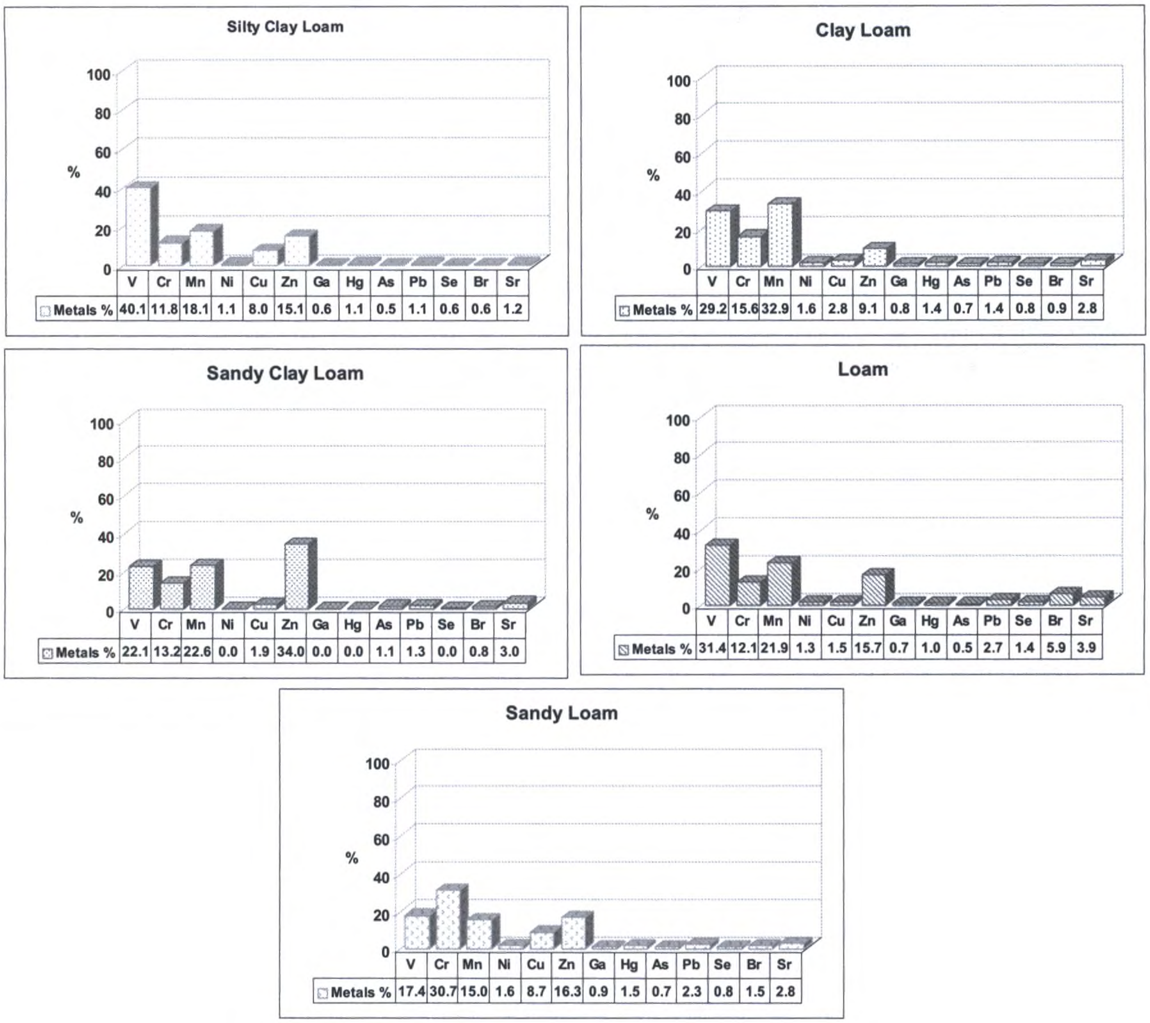


Figure 3. Composition of $PM_{2.5}$ soil dust from ambient samples. The insert shows the elemental signature of the five soil elements used to calculate the SOIL parameter.

Figure 4 shows the fractional concentrations of heavy metals (to their total). The concentrations of Cl, V, Cr, Mn, Cu and Zn vary according the soil type, but are detectable at 10 times the detection limit. Metals such as Ni, Hg, Pb, Br, As and Se are detectable, but are near the minimum detection limit. All are hazardous to human health and were detected in the $PM_{2.5}$ samples.

Conclusions

The composition of $PM_{2.5}$ dust raised from agricultural operations is quite similar across different soil types, being mostly mineral soil and organic matter. The split between mineral soil and organic matter varies slightly. Loam has a higher mineral soil and lower organic content, while silty clay loam is more evenly split. Other soil types lie between these two. The signature of the soil elements Al, Si, Ca, Ti, and Fe is very similar across all soil types, but the heavy metals signature is different for different soil types. Metals may be a natural component of the soil or they may arise from other sources in the San Joaquin Valley.



Silty Clay Loam

	V	Cr	Mn	Ni	Cu	Zn	Ga	Hg	As	Pb	Se	Br	Sr
Metals %	40.1	11.8	18.1	1.1	8.0	15.1	0.6	1.1	0.5	1.1	0.6	0.6	1.2

Clay Loam

	V	Cr	Mn	Ni	Cu	Zn	Ga	Hg	As	Pb	Se	Br	Sr
Metals %	29.2	15.6	32.9	1.6	2.8	9.1	0.8	1.4	0.7	1.4	0.8	0.9	2.8

Sandy Clay Loam

	V	Cr	Mn	Ni	Cu	Zn	Ga	Hg	As	Pb	Se	Br	Sr
Metals %	22.1	13.2	22.6	0.0	1.9	34.0	0.0	0.0	1.1	1.3	0.0	0.8	3.0

Loam

	V	Cr	Mn	Ni	Cu	Zn	Ga	Hg	As	Pb	Se	Br	Sr
Metals %	31.4	12.1	21.9	1.3	1.5	15.7	0.7	1.0	0.5	2.7	1.4	5.9	3.9

Sandy Loam

	V	Cr	Mn	Ni	Cu	Zn	Ga	Hg	As	Pb	Se	Br	Sr
Metals %	17.4	30.7	15.0	1.6	8.7	16.3	0.9	1.5	0.7	2.3	0.8	1.5	2.8

Figure 4. The signature of metals hazardous to human health for different soil types.

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Comparison of Measured Estimates of Annual Ammonia Emissions from Poultry Production Facilities with Mass Balance Modeling Approaches

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Abstract

Aerial ammonia is the predominant gaseous pollutant from poultry production facilities, resulting from microbial decomposition of uric acid in bird feces. These emissions are an important environmental issue as these emissions contribute to increased nitrogen deposition in land and aquatic environments, and as a precursor to atmospheric, fine particulates. Ammonia emissions have been monitored from broiler and egg laying production facilities over twelve to fifteen month periods in Kentucky, Pennsylvania, Iowa, Indiana, and North Carolina in recent years as part of USDA competitive grant funded projects. A report by the National Research Council (2003) found there was a need for the development of process based models with mass balance constraints of emissions. Undertaking a nitrogen balance on four, high-rise layer houses in Iowa, Liang et al (2005) showed that the residual error between nitrogen input and nitrogen outputs was less than 6% for any of the houses. In a study of a broiler house in Tennessee, Burns et al (2003) was able to able to obtain an estimate of ammonia emissions by mass balance modeling that was within 3% of the measured ammonia emission.

Estimates of manure production and characteristics are often used evaluating farm nutrient balances and determining the adequacy of land application areas. Sources of these estimates include published values by the American Society of Agricultural and Biological Engineers (ASABE), Midwest Plan Service (MWPS) and Natural Resources Conservation service (NRCS). The ASAE Standard D384.2 (2005) provides estimates of typical manure characteristics based on a mass balance modeling approach. Applegate et al. (2003) list a series of potential inaccuracies in this approach including that it is based on average diet formulations, limited nutrient retention values, assumptions and generalizations. Angel et al. (2003) compared the ASABE mass balance approach with the results of a biological mass balance on a mass balance broiler experiment and found that the ASABE model overestimated excretion of dry matter, nitrogen and phosphorus. A more flexible approach was used by McGahan (2002) in developing a worksheet based mass balance for broiler farms that allows customization of the diet nutrient composition, flock characteristics and uses carcass nutrient estimates rather than nutrient retention factors.

The study described in this paper was conducted at a site with four mechanically ventilated houses in central Kentucky. Each house was 12.2 m ×152.5 m. Houses were built in 1997. Each house had a 0.67-m opening along the full length of both sidewalls covered by a single layer curtain for emergency ventilation. There was an insulated ceiling in all houses. Ventilation fans included 8, 1.22-m diameter fans and 6, 0.92-m diameter fans in each house. Box inlets were located along both sidewalls and were automatically controlled based on static pressure differences. The ventilation system was controlled by individual thermostats and timers. Air temperature data were collected using a sensor positioned in the brooding area. The central half of the houses was used for brooding. All houses reused litter between flocks and performed one annual cleanout, with decaking between flocks. Broiler litter was characterized at the end of each flock. The brooding area of two of the houses was treated with poultry litter treatment, a chemical product (sodium hydrogen sulfate, $NaHSO_4$) that is applied to the litter prior to each flock to reduce the pH of litter. The number and type of birds placed alternated between 25,000 females placed at 13.44 birds/m^2 and grown for 54 days and 20,000 males placed at 10.75 birds/m^2 and grown for 64 days. The houses were

divided into 3 zones, nonbrooding (north end, 632 m^2), brooding (center, 706 m^2) and nonbrooding (south end, 520 m^2). The 8, 1.22-m diameter fans for tunnel ventilation were located in the south end.

For the data collected and reported here, ammonia emission rate (ER) was obtained from Portable Measuring Units (PMU) developed for the project. The PMU used two electro-chemical NH_3 sensors and an infrared CO_2 sensor. To avoid measurement errors caused by electro-chemical sensor saturation from continuous exposure to NH_3-laden air, cycles of 14 min purging with fresh outside air and 6 min sampling of exhaust air stream were used. This purging-sampling cycle resulted in 20 min measurement intervals. Complete details of the PMU are given in other references and not repeated here (Xin et al., 2002; Liang et al., 2005; Gates et al., 2005). One PMU was installed in each broiler house. The PMU was located near and monitored near the primary minimum ventilation timer fan used for cold weather ventilation. A second PMU was located on the first of the tunnel ventilation fans during warmer conditions when the house is likely to transition into tunnel ventilation mode. PMUs typically collected data at each house for about 48 h however, for one monitoring period, data collection exceeded 72 h. The interval between collection periods at a site was typically two or three weeks. A 'day' of data collection was nominally from noon of one day to noon of the following day.

Each house contained 14 exhaust ventilation fans. Each fan's ventilation capacity was determined with a Fan Assessment Numeration System (FANS) unit. The FANS incorporates an array of five propeller anemometers to perform a real-time traverse of the air flow entering fans of up to 1.37 m diameter. Details of the FANS unit's design and performance specifications are provided elsewhere (Gates et al., 2004; Wheeler et al., 2002). The FANS unit was used to evaluate each fan in all four of the broiler houses on this site. Fan on-off time was monitored using fan motor loggers. Average static pressure difference over the fan on-time interval was used to determine fan ventilation rate, using fan curves developed for each fan as determined from the FANS testing.

Based on the regression equations developed for each flock at this site during the monitoring period emission (Wheeler et al., 2004) and the methodology developed by Gates et al. (2005a) for assessing broiler house emissions, the ammonia emissions from the four houses at the KY-B site were calculated for the five flock period between cleanouts. The cumulative ammonia emission over the period was 23,484 kg, while the cumulative emission over time is presented in Figure 1.

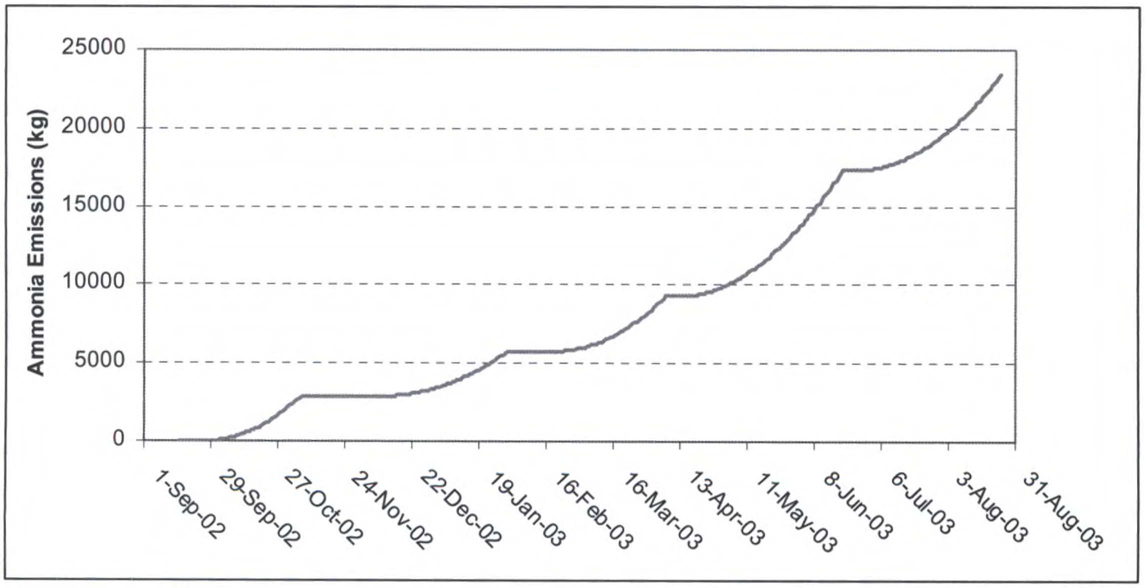

Figure 1. Cumulative ammonia emissions from Site KY-B with 4 broiler houses over 5 flocks in 1 annual cycle between litter clean-outs.

The litter in the brooding and non-brooding sections of the houses was separately sampled at the conclusion of each flock using the random walk method (Singh et al., 2004). A single composite sample was analyzed from each house section. Analyses included moisture content, pH, total ammoniacal nitrogen (TAN), total nitrogen (TN) and total phosphorus (TP).

A mass balance was constructed based on integrator records for numbers and weights of birds placed and removed, feed analysis and feed consumed, and farmer records of mortalities, sawdust placed and litter removed. The completed mass balance is shown as Table 1.

Category	Nitrogen (kg)
Birds In	514
Feed In	78034
Sawdust In	218
Total In	78765
Birds Out	35938
Mortalities	494
Litter Removed	18824
Ammonia Emitted	19340
Total Out	74593

The error in closure of mass balance is 5.6%, with nitrogen inputs exceeding measured nitrogen outputs by 4172 kg over the period of five flocks. Ammonia emission represents 24.6% of the total nitrogen input into the system or 24.7% of the non-bird nitrogen inputs into the system. Potential sources of error in the mass balance included assumptions on carcass analysis and determination of mass of litter removed. Potential losses that were not measured or accounted for include nitrogen loss in particulate emissions, as nitrous oxide and other gaseous nitrogen forms. Based on the total suspended particulate (TSP) emission factor determined by Lacey et al. (2003), and assuming that particulate nitrogen content is the same as the litter, the nitrogen loss as particulates would have been approximately 750 kg. Given the nature of the experiment, conducted on a commercial broiler production site, obtaining a mass balance closure with less than 6% error is deemed successful, thus supporting the ammonia emission estimates derived in the project.

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Carbon Dioxide and Nitrous Oxide Fluxes in Organic, No Till and Conventional Till Cropping Systems

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Abstract

The potential roles of organic and conventional cropping systems in mitigating current increases in atmospheric concentrations of carbon dioxide (CO_2) and nitrous oxide (N_2O) remain unclear. As part of a long-term study to evaluate the sustainability of organic and conventional cropping systems, we measured soil fluxes of CO_2 and N_2O in organic, no till and chisel till cropping systems. We measured gas fluxes on 24 and 27 dates in three field replicates in the corn phase of the three corn-soybean-wheat/legume crop rotations in 2004 and 2005, respectively. Cumulative CO_2 flux was greater in the organic (12.88 g CO_2 m^{-1} h^{-1}) than in the no till (8.62 g CO_2 m^{-1} h^{-1}) and chisel till (10.38 g CO_2 m^{-1} h^{-1}) systems in 2004. Differences among systems were due mostly to large CO_2 fluxes in spring in the organic system, especially following moldboard plow incorporation of a hairy vetch cover crop and disk incorporation of poultry litter. Rotary hoeing and cultivation in the organic system did not appear to have an effect on CO_2 flux, probably because readily available soil and vetch C had already been released in response to prior field operations. Soils in the no till system responded differently to changes in soil moisture than did soils in the organic system. Maximum CO_2 flux occurred at 20.0% VWC (~38.4% water filled pore space (WFPS)) in the organic system and at 27.6% VWC (~52.5% WFPS) in the no till system. These differences might be due to lower soil porosity and greater dissolved organic carbon in the organic compared to the no till system. Carbon inputs into the organic system were also greater than in the other two systems. Full assessment of net C balance will be conducted at the end of the 10th year of cropping, in 2006. We measured CO_2 flux using both static and dynamic methods on 17 dates in 2004 in the no till and organic systems. While both methods described the same overall patterns of CO_2 flux over time, the dynamic chambers gave almost consistently higher readings than the static chambers [static method = 0.458(dynamic method) + 0.128; r^2=0.71]. A fan, which might disrupt the boundary layer between the soil and the atmosphere, may have resulted in higher measured fluxes using the dynamic method. Results from CO_2 flux measurements for 2005 and N_2O data for both years are being analyzed and will also be presented.

Characterization of Skatole-Producing Microbial Populations in Enriched Swine Lagoon Slurry

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Abstract

Skatole is a potent odorant in animal waste produced by anaerobic degradation of L-tryptophan. Little is known of the biochemistry involved in skatole production, the phylogeny of skatole-producing microorganisms or the conditions that favor their growth. These deficiencies hamper attempts to reduce skatole production. Our goals were to enrich for skatole-producers in swine waste and evaluate the microbial community structure. We supplemented swine lagoon slurry with 100 μM L-tryptophan, indole pyruvic acid (IPA) or IAA. Control treatments received no additional substrate. GC-MS was used to measure indole and skatole production in the slurries. Very little indole (0.9 ± 0.02 μM) or skatole (1.8 ± 0.07 μM) was produced in the control over the course of the 14 day experiment. The final concentration of skatole was 50.4 ± 1.6 μM, 61.6 ± 1.1 μM and 68.4 ± 24.8 μM in the L-tryptophan, IPA, and IAA supplemented treatments, respectively. DGGE analysis was performed on DNA extracts from samples taken on days 0, 7 and 14 to evaluate changes in the microbial populations over time. The average number of bands or operational taxonomic units (OTU's) for samples from unsupplemented swine lagoon slurry taken on days 7 and 14 was lower than for any of the other treatments. OTU's increased in all supplemented treatments, with the greatest differences seen in samples supplemented with IPA or IAA. Future studies will evaluate phylogenetic differences in diluted populations having high skatole concentrations. Knowledge concerning the organisms producing this odorant should provide information vital to controlling microbes responsible for its production.

Introduction

In recent years, malodorous emissions from concentrated animal feeding operations (CAFOs) have been the source of complaints from rural neighbors and are receiving greater attention from regulatory agencies. Indole and 3-methylindole (skatole) are potent volatile compounds that are known to be responsible for some of the most offensive odors emitted from livestock wastes. These compounds are produced by anaerobic degradation of L-tryptophan in the intestine and in animal waste storage systems. The types and concentrations of the two products of tryptophan degradation depends on the maintenance of a low oxidation-reduction potential in the system, the availability of the amino acid (usually depending on diet), and the production of intermediate metabolites (Yokoyama & Carlson, 1979).

Indole is the most prevalent metabolite of tryptophan degradation, it is produced by a wide-range of bacterial species and much is known about its production and biochemical regulation (Deslandes *et al.,* 2001; Yokoyama & Carlson, 1979). However, skatole is the more powerful odorant, it has a low threshold for detection, it is responsible for boar taint in swine and acts as a pneumotoxin in cattle, goats, horses, rabbits, mice and rats, and may cause tissue damage in humans as well (Diaz *et al.,* 1999). Although skatole producers from two bacterial genera, *Lactobacillus* sp. and *Clostridium* sp., have been isolated from the intestines of livestock, very little is known about the microorganisms or the biochemical pathways leading to its production (Mackie *et al.,* 1998; Zhu, 2000).

Research has shown that the addition of intermediate indolic or aromatic compounds increases formation of skatole (Honeyfield & Carlson, 1990; Yokoyama & Carlson, 1979). Isolates produce skatole either directly or by decarboxylating indole-3-acetic acid (IAA) (Jensen *et al.,* 1995; Yokoyama & Carlson, 1981). In this study, the production of skatole from mixed microbial populations present in swine lagoon slurry was evaluated following supplementation with 100 μM of either tryptophan, indole acetic acid (IAA) or indole pyruvic acid (IPA) and incubating for 14 days in anaerobic conditions with un-enriched slurry serving as a control. The impact of these enrichments on the bacterial population was evaluated using denaturing gradient, gel electrophoresis (DGGE).

Materials and Methods

Sampling

Samples were collected from a swine waste lagoon in Bowling Green, Ky using a 2 L bucket attached to a pole. Water was collected below the lagoon surface, and strained through a double layer of cheesecloth under an atmosphere consisting of 95% CO_2, 5% H_2 in an anaerobic hood (Thermo Electron Corp., Waltham, MA). One hundred mL of filtered slurry was added to 125 mL serum bottles (I-Chem, Rockwood, TN) and supplemented with 100 µM of IAA, IPA, or tryptophan. Control samples received no supplemental substrate. One mL samples were removed from each vial for gas chromatographic analysis and one mL samples were taken for microbial community analysis on days 1, 2, 7 and 14. Each treatment was performed on triplicate samples.

Indole and Skatole Analyses

Twister® stir bars (10 by 3.2 mm- Gerstel USA, Baltimore MD) with a 1 mm PDMS coating were preconditioned for 1 hr at 250 ºC under a stream of high purity N_2. One mL samples from the vials were placed in 2 mL autosampler vials along with the stir bars/extractors, the vials closed, and the samples extracted from 1 h at 500 rpm at room temperature. Afterwards, the Twisters were removed from the vials, rinsed with deionized water, blotted dry, and placed in 17.8 cm mm long by 4 mm i.d. thermal desorption tubes (Supelco Inc.) and desorbed in a model

TDSA thermal desorption system (Gerstel USA). The stir bars were desorbed using an initial temperature of 25 ˚C with a delay time of 0.25 min. and then heated at 60 ˚C min^{-1} to 225 ˚C with a final time of 3 min. Desorbed volatiles were transferred by a heated transfer line maintained at 240 ˚C to a glass wool-packed injection liner maintained at -50 ˚C with liquid CO_2. Retained compounds were then transferred with a 20:1 split ratio to a 30 m by 0.25 mm Rtx-35 MS column (35% diphenyl-65% polydimethylsiloxane-Restek Corp., Bellefonte PA) with a film thickness of 0.25 µm by heating the injector at 10˚C min-1 to 300 ˚C with a final time of 3 min.

GC-MS was performed on a Varian Saturn 200 ion trap interfaced to a Varian model 3800 gas chromatograph (Varian Associates, Palo Alto, CA). GC operating conditions were: He carrier constant flow rate of 1 mL min^{-1}, column oven 55 ºC for 1 min, then programmed at 7 ºC min^{-1} to 100 ºC, and hence at 15 ºC min^{-1} to 295 ºC and held for 10 min, transfer line temperature 300 ˚C. The mass spectrometer was run in electron ionization mode with an emission current of 10 µamperes using a scan time of 0.35 sec per scan and a scan range of 45 to 225 amu.

DNA extraction from spiked lagoon samples

DNA was extracted from slurry (1.0 mL) using the Ultra Clean™ Soil DNA Isolation kit (MoBio Laboratories, Solana Beach, CA). Prior to extraction, samples were pelleted by centrifugation at 14,000 X g for 10 min. The pellet was then extracted according to manufacturers instructions, except bead tubes were placed in a Fast Prep FP120 (Q-BIOgene, Irvine, CA) for 30 s at a speed of 5.5 m/s instead of vortexing.

DGGE analysis of microbial populations

Total bacterial community DNA was amplified using the primers and DGGE conditions listed in Table 1. All PCR amplifications were performed in a PTC-200 DNA thermal cycler (MJ Research, Las Vegas, NV) as follows: initial denaturation at 94°C for 5 min, 10 cycles of touchdown PCR (94°C for 30 s, 61°C annealing for 30 s with an 0.5°C decrease/cycle, and extension at 72°C for 45 s), followed by 25 cycles at 94°C for 30 s, 60°C 30 s, and 72°C for 45 s, and a final extension step at 72 °C for 5 min. Sequences were amplified from 2 µl of extracted slurry template DNA using Ready-To-Go-PCR Beads (Amersham Pharmacia, Piscataway, NJ), with 800 nM each primer. Negative controls, containing all the components except DNA templates, were included in parallel. After PCR, 5 µl aliquots were subjected to agarose gel electrophoresis with 1.5% (wt/vol) agarose gels. Aliquots (20 µl) were resolved on polyacrylamide gels (37.5:1) containing a gradient of denaturants (100% denaturants consisting of 40% [vol/vol] formamide and

7 M urea) as indicated in Table 1. All the DGGE gels were run at 60°C and 82V for 15 hr, with a DCode Universal Mutation Detection system (Bio-Rad Laboratories, Hercules, Calif.). The DGGE gels were stained with Sybr Gold (Molecular Probes, Eugene, OR) according to the manufacturer's specifications, and the images were captured using a Foto Analyst Investigator Series Image Analysis System (Fotodyne, Hartland, WI).

Table 1. PCR and DGGE conditions used for visualization of swine lagoon slurry populations

Primer	Sequence (5' to 3')	Target Region[a]	Amplicon Length (bp)	DGGE Conditions[b]	Reference
-341f[c]	CCT ACG GGA GGC AGC AG	V3-V5	586	6.5%, 30-60%, 80V	Casamayor et al., 2000
907r	CCG TCA ATT CCT TTG AGT TT				

[a] Variable region within the *rrs* gene targeted by the primer set

[b] DGGE conditions=gel percentage, gradient range, voltage

[c] Primers with 40-bp GC clamp on the 5' end

GC clamp = CGC CCG CCG CGC CCC GCG CCC GTC CCG CCG CCC CCG CCC G

Results and Discussion

Metabolism of L-tryptophan, IPA and IAA in Mixed Community Swine Lagoon Slurry

Swine lagoon slurry either received no supplement or was supplemented with 100 µM L-tryptophan, IPA or IAA. Very little indole (0.9 ± 0.02 µM) or skatole (1.8 ± 0.07 µM) was produced in the control over the course of the 14 day experiment (Fig. 1). There was a 72 hour lag in production of both indole and skatole in all treatments. Indole was produced at significant concentrations only in the L-tryptophan supplemented treatments. Indole concentrations peaked on day 7 (18.5 ± 1.6 µM) and then decreased slightly by the end of the experiment (13.0 ± 1.2 µM). Skatole was produced to a greater extent in the slurries. Even in the L-tryptophan supplemented treatments, skatole production was almost 4 times greater than indole production (Fig. 1). Skatole production continued to increase over the course of the 14 day experiment. The final concentration of skatole was 50.4 ± 1.6 µM, 61.6 ± 1.1 µM and 68.4 ± 24.8 µM in the L-tryptophan, IPA, and IAA supplemented treatments, respectively (Fig. 1).

IAA supplemented treatments produced the greatest concentration of skatole. Yokoyama and Carlson (Yokoyama & Carlson, 1979) found that in the rumen skatole was produced by conversion of L-tryptophan to IAA followed by decarboxylation of IAA to form skatole. Jensen et al. (1995) found that pig fecal slurry populations also convert L-tryptophan to skatole by decarboxylation of IAA. In our experiments, we found that swine lagoon populations preferentially convert L-tryptophan to skatole rather than indole, presumably by a series of decarboxylation reactions with IAA as an intermediate.

IPA supplemented treatments also produced large amounts of skatole. In contrast to L-tryptophan supplemented slurries, however, the levels of indole were not noticeably different from those of control slurries. These results agree with those of Chung et al (1975), who found that intestinal anaerobe isolates formed IAA through indolepyruvic acid, following formation of IPA via transamination of L-tryptophan with α-ketoglutarate. However, the low level of indole produced was unexpected since IPA is the major intermediate in tryptophan degradation to indole. In the swine lagoon slurries used in this study, addition of IPA obviously drove the reaction toward skatole production.

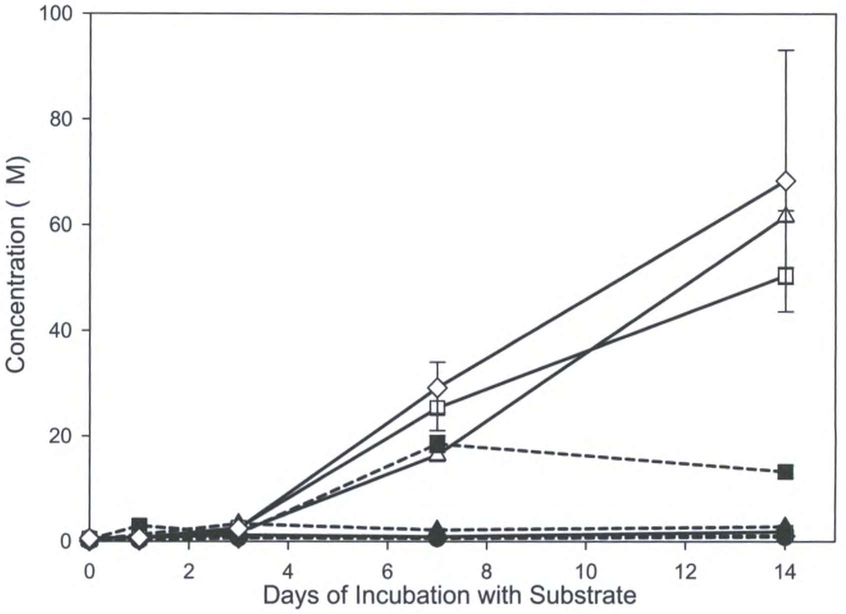

Figure 1. Plot of the concentration (µM) of Skatole (solid lines, open symbols) or Indole (dashed lines, solid symbols) for samples incubated without substrate (○) or with 100 µM IPA (△), 100 µM Tryptophan (□), or 100 µM IAA (◇) over the course of 14 days. Average and standard deviation of triplicate samples taken on days 0, 1, 3, 7 and 14.

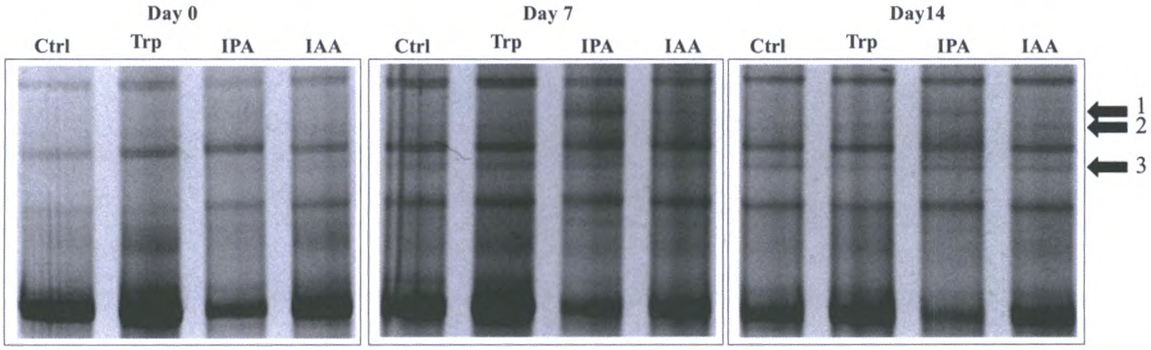

Figure 2. Negative image of Sybr Gold®-stained DGGE gels containing PCR-amplified 16S rDNA sequences from swine lagoon slurry samples. Arrows with numbers indicate bands that appeared after 7 days incubation with 100 µM substrate. Ctrl=control; Trp=Tryptophan; IPA=Indole pyruvic acid; IAA=Indole Acetic acid.

Analysis of Microbial Populations

DGGE analysis was performed on DNA extracts from samples taken on days 0, 7 and 14 using primers designed to target members of the *Bacteria* (Fig. 2). The average number of bands or operational taxonomic units (OTU's) for samples from un-supplemented swine lagoon slurry taken on days 7 and 14 was lower than for any of the other treatments. The IPA treatment had the most pronounced difference with one strong band (Fig. 2) appearing at day 7 and remaining through the end of the experiment. Similarly, the IAA treatments had an increase in the number of OTUs in both day 7 and day 14 samples (Fig. 2). Overall, patterns were very similar for all treatments with the four most intense bands present in all treatments. Using DGGE, populations that represent less than 1% of the total population are not likely to be detected (Casamayor *et al.,* 2000; Muyzer *et al.,* 1993). Therefore, the fact that the population profiles for spiked

IPA and IAA samples did change, suggests that there were significant changes in the microbial community. Preliminary data suggests that the major populations in these samples are *Bacteroides* sp. and *Clostridia* sp. (data not shown). Although species from both of these groups are common fecal commensals, species from both genera have been shown to produce IAA (obviously an important precursor to skatole formation) (Deslandes *et al.,* 2001) and species of *Clostridia* are among only a few known producers of skatole. Future work will focus on excision and sequencing of key bands from the DGGE profiles to obtain fundamental new information regarding species that are producing skatole in swine lagoon slurry.

Conclusions

In swine lagoon slurries, skatole production was enhanced by supplementation with the reaction intermediates, IAA and IPA. There was a 72 hour lag in skatole production in all treatments. This lag phase correlated with a visible shift in the DGGE profile of the microbial population in skatole-producing treatments. These results suggest that skatole production in swine lagoon systems depends on the presence and possibly on the concentration of at least three intermediate compounds: tryptophan, IPA and IAA. Shifts in the microbial population which occurred concomitant to skatole production may correlate to the build-up of populations necessary for production of essential intermediates and/or the skatole producing populations themselves. Future research will focus on phylogenetic characterization of the microbial population in skatole-producing communities. A better understanding of the populations that are instrumental in skatole-production should aid in uncovering methods for abating its formation in animal waste storage systems.

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Agriculture Air Emissions and Impacts in and Near the Umatilla Indian Reservation

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Introduction

The Confederated Tribes of the Umatilla Indian Reservation (CTUIR) is one of over 550 federally recognized Indian Tribes. The Confederation is made up of the Cayuse, Walla Walla and Umatilla Tribes with a total enrollment of about 2600 members. Their current reservation, the Umatilla Indian Reservation (UIR) is located in Umatilla County in Northeaster Oregon and consists of about 175,000 acres. In addition, members of the CTUIR are assured access to public lands for performing traditional practices within the millions of acres of land it ceded to the U.S. government in the Treaty of 1855. These practices include hunting, fishing, berry picking, gracing stock, gathering of medicines and other materials, and religious ceremonies. As with many of the Native American Tribes, the UIR is in a rural setting where agriculture, forestry and silvaculture are commonly found in and near the reservation and often the backbone of the economy (Table 1). The impact of agriculture, silviculture, and forestry on these natural resources and the freedom to practice a traditional life style without risk to human health from environmental contamination in the air and that spread (5) by the air has become alarming to indigenous peoples on many of the federally recognized tribes in the United States. The air emissions from agriculture, silviculture and forestry have until recently been largely outside the regulatory envelope of the Clean Air Act. Consequently little quantitative information is available regarding the types and amount of air emissions associated with these natural resource extraction businesses and their transport and fate in the ecosystem. These issues are identified and discussed from a tribal wisdom viewpoint of "natural relationships" - a viewpoint that air is an essential natural resource, just as food, water and energy; that all living things breathe air and are connected and interdependent; that the health and well being of the whole depends on each member and visa versa. Understanding and subscribing to this model of natural relationships is a corner stone of Traditional Native American wisdom, embodied in respecting and protecting "mother earth".

Table 1. 2004 Ag Statistics for Umatilla Co. and Umatilla Indian Reservation (1,2)

	Population	Total Acres	Harvested Acres Grain	Gross Grain Sales, $1000	Gross Farm Sales, $1000
Umatilla Co.	73,436	2,057,600	313,700	69,161	235,271
UIR	3,200	175,000	30,000	NA	NA
Oregon State	3,421,400	61,600,000	1,044,780	212,518	3,799,031

Natural Relationships Model

Traditional tribal wisdom teaches that all things, animate and inanimate, are connected and dependent upon one another, and that balance is important for health and well being. It is just this natural relationships model that is used by many Tribal communities in making policy decisions regarding their natural resources. The model demands a holistic assessment of salient factors before drawing conclusions and taking action. With respect to the subject we here are concerned with the footprint left by the anthropogenic sources of air emissions from the practice of agriculture and forestry.

In theory a mass balance as shown in equation 1 can be used to inventory and account for the flow and removal of individual and total emissions from agriculture and other practices to the air shed, where M_f is the mass released to the air shed, M_l is the mass leaving the air shed, M_r is the mass reacted in the air shed and M_a is the mass accumulated in the air shed. The amount of air pollutant in the air shed at any point, M_a, in time can be used to determine various risks to human health and the environment through various exposure, uptake and distribution mechanisms. While rather straight forward in principle, the approach suffers from incomplete and inaccurate data upon which to make the computations.

$$M_f - M_l - M_r = M_a \qquad (1)$$

The mass balance can be used in conjunction with the emission factor method, equation 2, to estimate the emission of individual pollutants, where E is the mass of a particular analyte emitted, A is the rate of its emission (mass/time), E_f is the emission factor, (1-ER/100) adjusts emission for emission control devices where ER is the efficiency of the device. Emission factors (E_f) have been compiled and regularly updated by EPA (3) for many different sources and types of air pollutants including those regulated under the NESHAP portion of the Clean Air Act, carbon monoxide, oxides of nitrogen, oxides of sulfur, and particulate matter.

$$E = A * E_f * (1\text{-}ER/100) \qquad (2)$$

Inventorying Sources of Air Emissions

There are a number of sources of information from which to build the inventory. County, state and federal agencies are a good source of statistical information as are local USDA/State Agriculture Experimental Stations. The information shown in Table 2 has been sequestered from these sources (1,2) and used in conjunction with the emission factor method to estimate the emissions from wheat production on the UIR.

There are approximately 60,000 acres of land on the UIR designated for crop production and the primary (> 95% est.) crop is non-irrigated wheat. The traditional practice of raising this crop is to have half of the land in production at any time allowing the other half to remain fallow for soil rejuvenation, so that there is about 30,000 acres in production a year. The principle activities associated with cropping wheat are listed in Table 2 along with the air emissions associated with each of the various activities in this agriculture production cycle using equation 2 and available emission factors (3).

Table 2. 2004 Estimated Air Emissions (lbs) Associated with Wheat Production on the UIR

Activity	**PM-10**	**PM-2.5**	**CO**	**NOx**	**SOx**	**HC/VOC**	**NH3**	**HAP**
plowing	101	11	113	432	11	20		
planting	51	6	57	216	5	10		
fetilizing	51	6	57	216	5	10	50,715	
pesticide/herbidice	101	11	113	432	11	16,406		16,406
harvesting	91	11	113	432	11	20		
field burning	303,072	287,232	3,537,072	123,024	24,816	286,176	70,224	
wind blown dust	600,000	60,000						
grain elevator	10,264	1,026						
transport to market	NA	NA	NA	NA	NA	NA		
Total, lbs	913,732	348,303	3,537,524	124,752	24,858	302,643	120,939	16,406

HAP, hazardous air pollutant the active ingredient in pesticide/herbicide. HC/VOC, hydrocarbon/volatile organic carbon.

Substantial quantities of otherwise regulated air pollutants are seen to be released to the air and since some of the activities listed occur in a short period of time, e.g., field burning, spraying, and fertilizing, local air quality impacts can be potentially significant. There is little regulatory control of these area sources, even though they exceed significant emission rates listed in Table 3 for point sources under the Clean Air Act.

Table 3. Significant Emissions Rates of Air Pollutants

Pollutant	Emission Rate (ton/yr)
CO	100
NOx	40
PM-10	15
VOC	40
SOx	40

Identifying, Quantifying, and Remediating Impacts

Further analysis is required to determine the impacts of agriculture and forestry practices on health and well being. The emissions inventory has shown the potential for large quantities of regulated air emissions from just one of the many different agriculture and forestry practices. Others may have as large emissions.

Monitoring data is needed to substantiate emissions estimates and determine concentrations from which human exposure and other impacts can be assessed. The emission inventory can be used in conjunction with the monitoring data to assess trans-boundary contributions to air quality on the UIR as well. The geography and weather patterns of the UIR are conducive to holding pollutants in the air-shed, providing the potential for the air pollution from a number of large upwind industrial sources to collect and react with those generated locally. Some regulatory relief is on the way to the CTUIR in the form of the Federal Air Rules for Indian Reservations that were recently promulgated by EPA (4). These rules will provide regulatory authority for Native American Tribes in the states of Oregon, Washington and Idaho.

Conclusions

Using a model of natural relationships we are directed to consider all the impacts. Such an approach makes us more responsible and protective of our environment and natural resources. This precursory holistic look at the impact of an agriculture practice has shown it to be a significant contributor to air pollution on the UIR. Those people and the ecosystems closest to the sources will generally feel the greatest impact. Further analysis and study will be required to quantify those impacts. Other agriculture and forestry practices may also be impacting air quality and other natural resources essential to the CTUIR's well being. These impacts may be larger than heretofore recognized.

The implication of these results are that the cost of products from agriculture and forestry to are much greater than currently accounted for in the product price, and further that better technology and methodologies are needed and regulations implemented to mitigate this situation, including public outreach and education. The people living in rural agriculture areas may well be bearing a disproportionate share of the hidden costs of agriculture and forestry.

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Identifying and Addressing Social Constraints Involved With the Use of Prescribed Fire in Forest Ecosystems of the Ouachita and Ozark Regions in Arkansas

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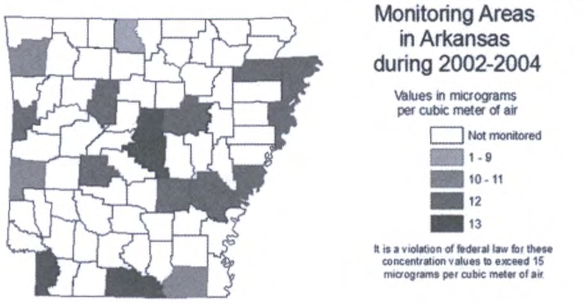
Abstract

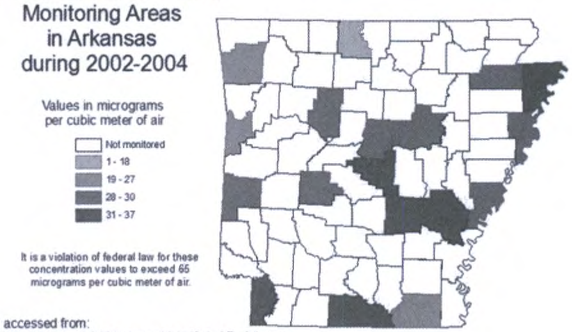
Fire is a key ecological feature of forest ecosystems in the Southern United States and Arkansas. Stanturf et al. 2002 indicated that "other than land clearing for urban development, no disturbance is more common in southern forests than fire". Fire as a result of natural and/or historical anthropogenic sources has undoubtedly shaped the composition and structure of current forests in Arkansas. Historically, fires from natural sources as well as Native Americans and Euro-American settlers have favored the establishment of fire adapted forest ecosystems in Arkansas. Fire was extensively used in land clearing for agricultural crops, to increase visibility, as well as to increase forage production for game and/or domesticated animals by Native Americans and early Euro-American settlers (Stanturf et al. 2002). Fire return intervals or the length of time between successive fires within the Boston Mountains of Arkansas have been estimated to be between 4.6-16 years prior to European settlement (1680-1820), 2.0-3.1 years during Euro-American settlement (1821-1880), and 1.4 -5.0 years during the region's developmental (1881-1920) period (Guyette and Spetich 2002). Following the establishment of the Ouachita and Ozark National Forests as well as the passage of the Clarke-McNary Act of 1924, which provided federal funding to states for fire suppression, the use of fire decreased in the northern and western portions of Arkansas. Guyette and Spetich (2002) reported that fire return intervals increased from less than a decade to in excess of four or more decades following 1920. With the suppression of fire, the forests of the Ouachita and Ozark mountains have again changed. Spetich (2004) indicated that the removal of fire from ecosystems in northern Arkansas has reduced the regeneration and establishment of oaks and thereby favoring non-fire adapted species. Removal of fire which maintained open shortleaf pine stands with abundant diverse forb/grass communities in the Ouachita Mountains has favored closed canopy stands with dense hardwood understories (Wilson et al. 1995). Changes such as these have negatively impacted populations of a number of animals that depended on these lost habitats (Bukenhofer and Hedrick 1997).

The recognition of the detrimental effects of fire removal has led to the reintroduction of fire to forest ecosystems of Arkansas. In 2004, over 300,000 acres of land was burned in Arkansas using prescribed fire (personal communication, Lawrence Holm Arkansas Forest Commission) and land mangers are dramatically increasing the use of prescribed fires to 1) restore fire-dependent ecosystems that have been lost due to fire suppression, 2) protect endangered species, and 3) promote healthy forests. Current proposed land and resources management plans in Ouachita and Ozark National Forests include projected average annual increases in prescribed fires totaling 101,000 acres or an increase of 140% over current burning levels (USDAFS 2005a; USDAFS 2005b). A consortium of federal and state agencies have also formed to develop large restoration areas that utilize prescribed fire and other silvicultural techniques to demonstrate the feasibility of and potential for large multiple landowner scale forest restoration (Anderson et al. 2003).

Although prescribed fire is critical for restoring and maintaining healthy forests, particulates in smoke can pose a risk to public health and welfare. Particulates less than 2.5 micrometers (PM 2.5) are associated with human health problems and are the primary particulate constituent of prescribe fires (McMahon 1999). The Clean Air Act (CAA) in 1970 authorized national air quality standards to minimize health risks. Areas that do not meet these standards (termed nonattainment areas) are required to mitigate emissions. Currently no 'nonattainment areas' occur in Arkansas but heavily populated counties such as Pulaski, Faulkner, Garland, and Washington (Figure 1) have elevated levels of PM 2.5 and are located near the boundaries of the Ouachita and Ozark National Forest. Air quality in these population centers could be negatively impacted by large scale increases in prescribed burning. Other sensitive areas in Arkansas include the Buffalo National River (Ozark Mountains) and the Caney Creek Wilderness (Ouachita Mountains). The CAA prohibits visual impairment within the wilderness and park boundaries. Thus land management policies designed to modify forest ecosystems with fire at times clash with environmental policy to protect air quality.

Figure 1. Historic <2.5 µm particulate matter emissions for Arkansas


Highest Annual Average 24-Hour Values for PM2.5 Monitoring Areas in Arkansas during 2002-2004


Highest 98th Percentile 24-hour values for PM2.5 Monitoring Areas in Arkansas during 2002-2004

Data accessed from: http://www.epa.gov/air/data/repsst.html?st~AR~Arkansas under the Criteria Air Pollutants/Report/Monitor Values headings

Recent fires and plans for increased use of fires have brought to the surface these inherent conflicts. For example, the Sierra Club has rejected the need for prescribed fire (Sierra Club-Arkansas Chapter 2004) and some members have advocated that the National Forest Service only wishes to use fire to increase timber harvests in Arkansas (Arkansas Democrat Gazette 2005a). In addition the health practitioners and residents of urban areas are becoming concerned with the effects of smoke from prescribed fire (Arkansas Democrat Gazette 2005b). Smoke from prescribed fires during 2004 impacted some of the most rapidly growing urban areas in Northwestern Arkansas such as Fayetteville, Rogers, and Springdale (Arkansas Democrat Gazette 2005c). Given the increased level of burning and concerns regarding prescribed fire disputes arising from the use of fire could become as volatile as the fires themselves. Ultimately these types of disputes could result in a reduction in the ability of land managers to use prescribed fire or result in costly air quality mitigation by government agencies. A better understanding of stakeholder concerns, attitudes, and beliefs relating to prescribed fire is needed to minimize potential disputes among stakeholder groups. In addition, dissemination of this information is needed to create a foundation upon which open discussions between divergent stakeholder groups can take place and provide infrastructure for solving disputes related to the application of fire as a land management tool.

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First Biomonitoring Study of Agricultural Originating Atmospheric Pollutants in Romania

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Abstract

Monitoring heavy metals (HM) and persistent organic pollutants (POPs) from the atmosphere has been continuously improved, biomonitoring being a topical method to assess their occurrence in the atmosphere. Eastern Romania (province of Moldavia) is characterized mainly by plain relief, facilitating intensive agricultural activities: vineyards, orchards, crop cultivation and animal farming. In this area the moss-monitoring technique was firstly introduced in 2000, to evaluate the atmospheric heavy metal deposition. The study was followed within the catchment of the Prut River (~11000 km^2), an important transboundary river, and then repeated in 2001. In 2002, the sampling network was extended over the whole province of Moldavia (~45000 km^2). Samples of the epiphytic moss *Hypnum cupressiforme* were collected at a total of 44 sampling sites in rural areas and V, Cr, Ni, Cu, Zn, As, Mo, Cd, In, Tl, Pb and Bi were determined by ICP-MS. Principal component analysis was used to identify possible sources of metals in moss. One of the main factors represents agricultural activities (mainly Cu and Zn). The spatial distribution of Cu reflects local agricultural sources with high concentration in the areas with extended vineyards. The local high concentration of Zn in some areas is most probably associated with the use of Zn based insecticides for fruit trees and fungicides for fruits, as this area has many orchards. The temporal trend shows varying deposition values for metals from agricultural activities, possible due to different seasonal agricultural treatments. In 2005 moss samples were collected in order to evaluate atmospheric contamination with HM and selected POPs, as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) with emphasis on agricultural emissions. In addition to 2002 sampling sites, moss samples were collected in the nearest vicinity of several important animal farms. Samples of surface soil, feedingstuffs, cow blood, meat and dairy products from these farms were also analyzed an d results were correlated with the moss data. All samples showed a relatively low contamination with OCPs and PCBs. Higher levels were found in dairy products and cow meat (up to 85 and 120 ng/g lipid weight for sum HCHs and sum DDTs). This is the first study of atmospheric contamination from agricultural sources in Romania. It gives an overview of the contribution of these sources to the general pollution level in one of the most important agricultural areas in the country. The obtained results are a very useful database of HM and POPs for future surveys.

Nitrogen Deposition via Atmosphera in Rural Zones in Cuba

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Abstract

The transboundary problems of global and regional atmospheric pollution are at current time, so our region is not considered as an exception on this matter. Acid deposition remains an important environmental issue in Europe and North America. Furthermore, it is emerging in new geographical areas, including parts of South/Central America, eastern and southern Asia and southern Africa. In these areas, emissions of nitrogen oxides are increasing rapidly as industrialization proceeds and the use of fossil fuels increases. In Cuba, main atmospheric nitrogen deposition compounds varies approximately from 19,0 to 70,0 kgN/ha.year in the rural place. The oxidized nitrogen forms being provided more 20% and wet deposition depends on our tropical rain climate features. The NH_3 and ammonium are the most important elements in our tropical conditions. This paper is showing more relevant results about main compounds of atmospheric nitrogen in Cuba from analysis of one long time series of data (more fifteen years) and its potential impact on agriculture.

WATER9 – An Air Emission Model for Animal Feeding Operations – Software for Both Field Agents and Comprehensive Scientific Research

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Abstract

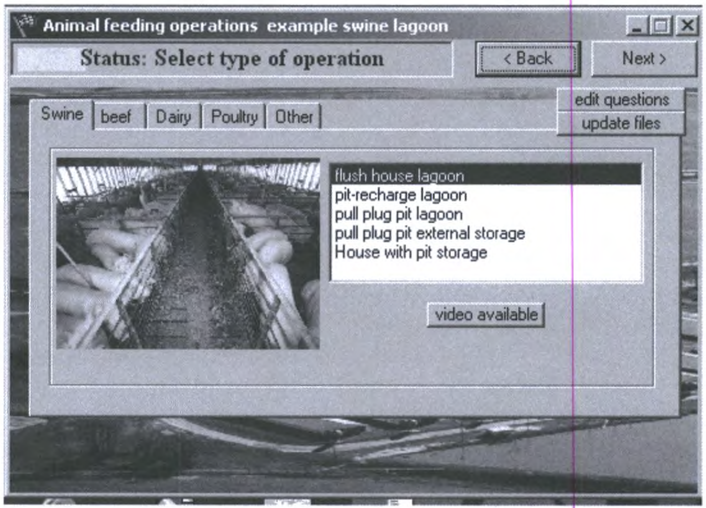
In response to the National Academy of Science's Board on Agriculture and Natural Resources and their Ad Hoc Committee on Air Emissions from Animal Feeding Operations' (AFO) October 2003 final report "Air emissions from Animal Feeding Operations: Current Knowledge Future Needs", RTI has supported the U.S. Environmental Protection Agency in evaluating adaptations of the software program WATER9 as a potential tool for use in providing scientifically sound estimates of air emissions from AFOs. The committee recommended EPA and USDA use such model(s) with mass balance constraints for nitrogen-containing compounds, methane, and hydrogen sulfide and adapt current or adopt new programs to fill gaps in research to improve process-based models to increase the accuracy and simplicity of measuring and predicting AFO emissions. In the 1990s, EPA contracted RTI to develop an emission model known as WATER9 for other rulemaking efforts such as estimating volatile organic emissions from hazardous waste management processes. Since that time, earlier versions of WATER9 have evolved to model other emission sources, including biological treatment tanks and trickling filters, as well as gases that include hydrogen sulfide. RTI has supported EPA in adapting WATER9 to predict AFO emissions by identifying and collecting the necessary input data on poultry, beef, dairy, and swine for WATER9's adaptation and by starting development of software to estimate ammonia, hydrogen sulfide, volatile organic and methane emissions from housing, lagoons, pits, and spray fields, among other sources. Should EPA and USDA adopt the model for this purpose, the current version of WATER9 for AFOs will be available in both a comprehensive modeling package as well as a field package that would enable field agents to assist growers with on-site nutrient management planning. This paper highlights the features of WATER9, its benefits, validation, and flexibility.

Introduction

The National Academy of Science's Committee on Air Emissions from Animal Feeding Operations in its 2003 final report AAir Emissions from Animal Feeding Operations: Current Knowledge, Future Needs@ stated that Aprocess-based modeling will help provide scientifically sound estimates of air emissions from AFOs for use in regulatory and [waste] management programs@ (NAS. 2003). The Committee recommended U.S. Environmental Protection Agency (EPA) and U.S. Department of Agriculture (USDA) use such model(s) with mass balance constraints for nitrogen-containing compounds, methane, and hydrogen sulfide; investigate the potential use of a process-based model to estimate mass emissions of odorous compounds; and adapt current or adopt new programs to fill gaps in research to improve process-based models to increase the accuracy and simplicity of measuring and predicting AFO emissions. The EPA, with support from RTI International, is evaluating WATER9, along with other process-based models, to address the NAS finding. WATER9 is a Windows-based computer program that estimates air emissions of individual waste constituents in wastewater collection, storage, treatment, and disposal processes. The model=s successful applications include the estimation of volatile organic emissions from hazardous waste management processes such as process vents, lagoons, and open storage tanks (see 40 CFR 264, subparts AA, BB, and CC). Since that time, WATER9 precursors have evolved to model a variety of emission sources, including biological treatment tanks, trickling filters, and cooling towers, as well as gases that include hydrogen sulfide. (See http://www.epa.gov/ttn/chief/software/water/index.html) This paper presents WATER9's adaptation for use as a tool for AFOs.

Features

WATER9 for AFOs contains a variety of features to enable a comprehensive estimation of emissions from animal waste generation, storage, transfer, treatment, and disposal operations. The current version predicts emissions of ammonia, volatile organic compounds, Clean Air Act hazardous air pollutants, hydrogen sulfide, nitrogen, nitrogen oxides (NO and N_2O), and carbon dioxide. It is capable of evaluating several livestock industries, including swine, poultry, beef, and dairy. Formal model features include the effects of surface area, temperature and wind, animal type and age, and design changes; a combination of removal mechanisms, including biodegradation, and chemical conversion and volatilization; pH effects; and effluent removal. Specific components have been designed for different types of animal confinement structures, feedlots, collection systems, waste piles, pits, impoundments, and land application units. The model can be used to predict the performance of crop uptake or air emission control devices. WATER9 uses proven correlations to calculate mass transfer coefficients and process unit input parameters to estimate emissions. WATER9's most important database is its extensive agricultural input information that includes waste generation rate by animal, waste characterization, properties of nitrogen, urea, uric acid and other waste constituents and by products. The user can adapt or add to these files. In addition, WATER9 features a Help file that describes, on command, AFO operations, advises on input values, animal and waste characterizations, case studies, and documents the model's validation. Active internet links are embedded in the Help file for the user, as well as a key word search function to expedite assistance. An added feature is the prediction of hydrogen sulfide bubble burst effects – an episodic condition that can threaten both the worker and the animal population. WATER9 reports in summary or detailed, unit-specific output, and it is amenable to designing new report formats.



Status: Select type of operation

Figure 1. WATER9 for AFOs offers a variety of menus for customizing emission modeling (example screen shot).

Benefits

WATER9 for AFOs is more beneficial than routine use of emission factors because it computes unit specific and system-wide mass balance of waste constituents from point of generation through environmental release. It allows the user to calculate site-specific emissions, using the local AFO's design and operating parameters. Waste management unit emission estimates account not only for local meteorological conditions such as wind and temperature, but also unit dimensions, operating rates, mixing, and biodegradation rates. In sum, WATER9 provides the evaluation of AFO system effects on the physical/chemical/biological behavior of waste constituents.

Validation

WATER9's performance has been validated for nonagricultural applications during its more than 15 years of development for EPA (http://www.epa.gov/ttn/chief/software/water/index.html) and application by multiple industries. WATER9 for AFOs validation began in 2004 with testing of individual components based on research in the literature as well as comparisons to flux chamber monitoring studies of lagoon emissions. (Aneja et al. 2005) WATER9 for AFOs will continue to benefit from new data generated via the 2005 CAFO national consent agreement's monitoring program.

Flexibility

Two versions of WATER9 for AFOs have been developed to accommodate the diverse audience of potential users. *WATER9 AFO - Full Capability* is a version designed for full flexibility in-process modeling. Users can adjust waste properties and detailed design and operating parameters. This version allows the users to enter/adjust all inputs and is valuable for scientific and engineering research as well as regional and nationwide research for policymaking.

The *WATER9 – Field* is a version developed with the grower and certified waste and nutrient managers in mind. It serves as tool for field use when designing a site and developing site-specific waste and nutrient management plans. The field version does not require special software training. It is designed in an Interview-Answer format to expedite outcome. The field version starts by selecting the type of operation to be evaluated or planned. *WATER9 - Field* leads the user through a series of questions and allows the user to enter the most important information about the site. It helps the user answer technical questions and, when desired, provides multiple choices and conversion factor aide. *WATER9 - Field* runs WATER9 for AFOs in the background and can provide a summary report well-suited for the grower and certified planners.

Conclusions

WATER9 is being evaluated by EPA as a potential tool for use in addressing the need for a mass balance model for AFOs. Based on EPA's WATER9 model which has been successfully applied in multiple industrial waste management settings, WATER9 for AFOs can enable both comprehensive modeling as well as affordable, convenient field modeling.

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Evaluation and Discussion of Ambient Ammonia Monitoring Networks and How They Can Benefit Regional Haze Reduction Planning

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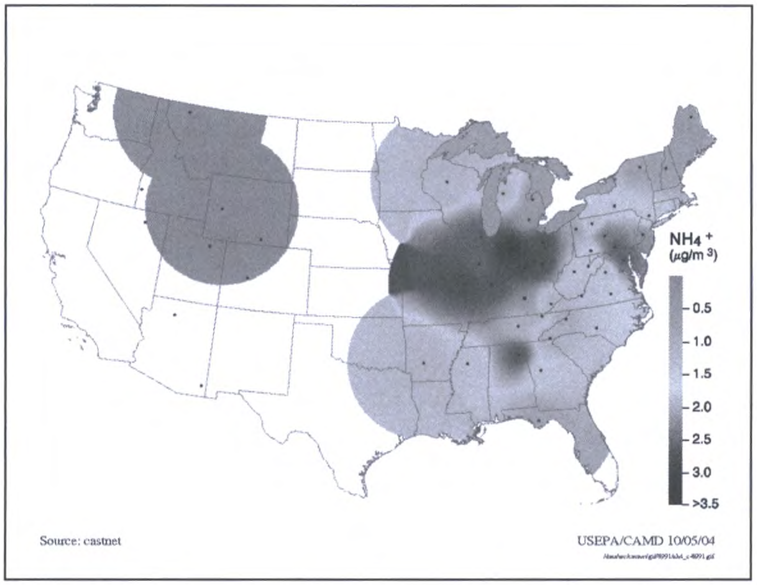
Abstract

Agricultural releases (animal husbandry and crop fertilization) generally account for 80 percent or more of the total ammonia emissions. Ammonia is critical in the secondary formation of fine particulate matter ($PM_{2.5}$). However, there are few ambient air monitoring stations that routinely measure ammonia gas concentrations. Characterization of ammonia in the atmosphere is particularly important because of the uncertainties in the reaction kinetics associated with ammonium salt particulate formation. Most atmospheric chemistry models use equilibrium assumptions, but available data indicate non-equilibrium conditions often exist near high ammonia emitting sources (i.e., agricultural lands). Therefore, accurate ambient ammonia concentration data are needed not only to assess the accuracy of the ammonia emission inventory from agricultural releases, but also to ground-truth atmospheric chemistry models used to estimate $PM_{2.5}$ formation. In 2005, the Central Regional Air Planning Association (CENRAP) operated the only long-term ammonia monitoring network in the U.S. RTI was contracted by CENRAP to review existing ammonia monitoring techniques and ammonia monitoring networks employed internationally and provide recommendations for improving the CENRAP ammonia monitoring network. This paper summarizes the findings of this research and discusses the advantages and disadvantages of the ammonia monitoring systems identified in terms of accuracy, biases, temporal specificity, and costs.

Introduction

Visibility in parts of the U.S. is being reduced by a condition known as "regional haze". Regional haze is caused by the presence of both natural and manmade particulates in the atmosphere that absorb or diffract sunlight. Regional haze may be composed of naturally occurring inorganic particulates; carbon particulates from combustion sources that include coal fired utilities, diesel engines, and agricultural burning; acid aerosols from manufacturing operations; and sulfate and nitrate salts of ammonium (NH^{4+}), potassium, and sodium. Ammonium salt particulates in regional haze can result from natural, animal, and manmade ammonia (NH_3) emission sources such as intensive animal feedlots (USEPA, 2004), crop fertilization, and automobiles. Ammonia's conversion from gas to aerosol particulate depends on the availability of sulfur dioxide and nitrogen dioxide pollutants in the atmosphere. Characterization of ammonia in regional haze is particularly important to developing better regional strategies to reduce haze (NAS, 2004).

Because the pollutants that lead to regional haze can originate from sources located across broad geographic areas, EPA has encouraged states and Tribal Nations across the U.S. to address visibility impairment from a regional perspective (USEPA, 2005). CENRAP is one of these regional planning organizations that is particularly interested in ammonia emission sources (see Figure 1). RTI International was contracted to review existing ammonia monitoring techniques and ammonia monitoring networks employed internationally and provide recommendations for improving the CENRAP ammonia monitoring network (RTI, 2005). This paper summarizes our approach, findings, and recommendations, noting advantages and disadvantages of the monitoring systems identified in terms of ammonia emissions inventories, atmospheric modeling, accuracy, biases, temporal specificity, and costs.



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USEPA/CAMD 10/05/04

Figure 1. 2004 deposition of ammonium in the United States

Method

Existing data from emissions inventories, modeling, and monitoring studies were analyzed to assess the correlation qualitatively between ammonia and regional haze in order to provide recommendations regarding future ammonia monitoring in the CENRAP region. First, RTI conducted an extensive literature review for ammonia emissions inventories, atmospheric modeling, and monitoring programs. Second, RTI performed a systematic metaevaluation on the information gathered to compare and contrast different inventory, modeling, and monitoring methods.

Results and Discussion

Ammonia Emission Inventories

Much of the literature reviewed described emission inventory methods and emission factors for specific ammonia emission sources. RTI assumed that CENRAP states generally employed the Carnegie Mellon University (CMU) Ammonia Model modified as per the recommendations from Sonoma Technology, Inc. (STI) (Coe and Reid 2003, Reid et al. 2004). Inventory conclusions by source category are described below:

- Animal feedlot ammonia emissions: RTI found that a process-based model eliminates the need to select the most appropriate annual average emission factor for a given animal type – a practice used in the CMU model. Given the widely varying climates represented by the CENRAP states, selecting a single emission factor solely based on the animal type and manure management train from the entire region is prone to large uncertainties.
- Fertilizer application emission inventory: The CMU ammonia model appears to be adequate for estimating ammonia emissions from fertilizer application. The draft report from Battye and Barrows (2004) when finalized will likely become the primary source of emission factors for fertilizer application, as well as the hourly temporal allocation of factors for fertilized soils.
- Natural landscapes emission inventory: Biogenic sources have been indicated to be an area of high uncertainty, so particular effort was made to identify appropriate emission factors for these sources. Using the CMU ammonia model version 3.06, biogenic sources contribute roughly 50 percent of the (non-point source) ammonia emissions in the CENRAP region. However, the report by Battye and Barrows, when finalized, is expected to become the primary source of emission estimates from natural landscapes. The authors present a model for estimating the

emissions from natural landscapes and for estimating the net ammonia flux for the natural landscape by using a deposition model. The key point for the emission inventory side of the equation is to estimate the gross emissions from these natural landscapes, not the net emissions. Many inventories neglect biogenic sources because they often act as ammonia sinks. However, atmospheric models require the gross emissions as their input, and the atmospheric model will calculate the deposition rate to assess whether the biogenic sources are net sinks or sources. By excluding these potentially significant source terms, subsequent modeling of these natural landscape areas could be biased low for ammonia.

- Motor vehicle emission inventory: With the advent of 3-way catalytic converters to reduce NO_x emissions, light-duty vehicles have become an important contributor to the ammonia emission inventory, especially for urban areas. New emission factors are significantly higher than those used in previous emission inventories, and the significance of these higher ammonia emissions, being co-located with emission sources of NO_x and SO_2, may be critical to consider in developing SIPs for achieving $PM_{2.5}$ attainment goals.

Atmospheric Modeling

RTI reviewed current atmospheric modeling being conducted by CENRAP and concluded that the CENAP monitoring network is able to supply most of the data needs of the models, including gas phase ammonia and nitric acid which are the two species that most other networks do not provide. Although the Community Multiscale Air Quality Model (CMAQ) is the standard EPA model, RTI understands the desire to evaluate less computationally intensive models.

In previous literature reviews to identify reaction rate kinetics for important ammonia gas-to-ammonium particle conversion processes, we had found no data. In the current literature review, we found that Baek et al. (2004) reported reaction rate constants for ammonia and sulfuric and nitric acid. The calculation of these reaction rate constants is dependent on a variety of assumptions, and therefore, may have significant uncertainties.

Ammonia Monitoring Methods

RTI's literature search was designed to locate ammonia sampling or monitoring methods in the U.S. and Europe during the period 2000 to the present. Monitoring/sampling methods were grouped into four classes:

1. *Passive samplers (six identified).* Passive samplers require no active pump or electrical power. Air is drawn into the sampler by the process of diffusion. Passive samplers may be exposed for periods of less than an hour to several weeks, depending on the concentration.
2. *Active samplers (three identified).* These systems use pumps to draw ambient air at a known flow rate through a filter (or filter pack) or across denuder surfaces. When sampling is complete (generally after a period of hours or days), the absorbing media is packaged and taken to a fixed laboratory for extraction and chemical analysis.
3. *Continual or continuous samplers (eleven identified).* This type of monitor is designed to sample the air on a continual (for instance, every 2 to 60 minutes) or continuous (constant) basis and report NH_3 and/or other atmospheric components on-site without the need for a laboratory. Spectroscopic or automated wet chemistry methods are usually employed.
4. *Other type samplers (two identified).* Technologies such as electrochemical sensors and surrogate sampling surfaces are grouped here.

Table 1 provides examples of each class of sampler, the analytical method used, the typical sampling duration, and (when available) the accuracy, precision, applicable range of concentrations.

Table 1. Example Ambient Air Sampling and Analysis Methods for Ammonia

Ambient Air ammonia Sampling Method	**Description of sampling method and analytical finish**	**Typical sampling duration**	**Accuracy (% different from reference)**	**Precision (%RSD)**	**Range and detectability**
Passive Samplers					
Ogawa	Teflon cylinder with 2 non-connected openings, each containing a reactive glass-fiber soaked in citric acid solution. Diffusion barrier caps at each end. Analysis of NH_4^+ by IC or colorimetry	One month	Results comparable to gas scrubber method	5 to 10%	<1ug NH_3/m^3
Active Samplers					
Manual diffusion denuder system	URG components. Teflon-coated cyclone, 2 denuders, Teflon and nylon filters. 11 L/min. Colorimetry and IC.	24-hr integrated sample	10 to 20% depending on ambient concentration	20 to 100% depending on ambient concentration	<50 ppt to source levels <50 ppt in air
Continual or Continuous Samplers					
MARGA multipollutant sampler	Monitoring instrument of aerosols and gases based on continual collection of gases and aerosols and routing for on-site analysis by ion chromatography. Utilizes a rotating denuder to remove gases and a steam chamber to grow, condense, and dissolve particles.	1-hr sampling; minimum is 20 min.	Initial tests show agreement within 20% with denuder/filterpacks for all gases, ions.	Tests underway	Tests underway
Other Type Samplers					
Surrogate surface approaches for NH_3 and NH_4^+	Dry deposition samples are collected on an aerodynamically smooth water surface and a knife-edge surrogate surface.	12 to 24 hr	Water surface sampling for NHx where $NHx = NH_3 + NH_4^+$); citric acid coated paper on a knife-edge surface (NHx); grease strip on knife edge (NH_4^+); IC analysis of extracts		Used in a range of 0.5 to 14 ug/m^3

Passive Samplers

The Ogawa sampler seems to be best characterized (Roadman et al., 2003). It has been used in a wide range of applications to detect ammonia concentrations ranging from less than 1 microgram per cubic meter ($\mu g/m^3$) in rural air (away from point sources) to 10 milligrams per cubic meter (mg/m^3) at concentrated animal feeding operations (CAFOs). A noteworthy feature of the membrane diffusion tube sampler is its use of sulfuric acid absorption solution, making it unnecessary to extract NH_4^+ from a filter in the laboratory. Passive samplers are most useful when average ammonia concentrations are at least 1 to 2 $\mu g/m^3$. Typical sampling durations vary from as little as five to ten minutes (when used at CAFOs) to a month (in rural areas, away from known ammonia sources). Passive samplers are often used to "saturate" an area to estimate the distribution of ammonia concentrations or to detect variations in concentrations upwind, in, and downwind of CAFOs.

Active Samplers

Active samplers cost from $5,000 to $20,000 to install and start up. The current CENRAP monitoring network uses the manual diffusion denuder system. It is assembled from components supplied by URG, Inc (Caughey and Gay, 2004; Kenski, et al., 2004). The commercially available Rupprecht & Patashnick (R&P) Model 2300 automatic speciation sampler uses honeycomb glass denuders and accomplishes the same measurements manual diffusion denuder system (R&P, 2003). Both systems can collect, in addition to ammonia, acidic gases such as SO_2 and HNO_3, and size-selected particles (usually $PM_{2.5}$) for analysis of additional anions and cations. The denuder systems integrates an air sample, usually for a period of from 12 to 24 hours. The low-flow diffusion Denuder for Long Term Ammonia (DELTA) is presently being used in the U.K. for long-term sampling (Sutton et al., 2001). The DELTA's low air flow (0.35 liters per minute [L/min] versus 10 to 11 L/min for the other systems) allows it to integrate a sample for up to a month. The DELTA system also collects NH_4^+ ions.

Continual or Continuous Samplers

These systems all cost $17,000 or much more and have continuing operations costs. The Monitoring Instrument for Aerosols and Gases (MARGA), gas and aerosol monitoring system (GAMS), and Dasgupta Texas Tech systems are all essentially automated wet chemistry laboratories for extraction of denuder samplers for acidic and basic gases and for solubilization and ion chromatography analysis of particle composition (Buijsman et al., 1998; Löflund et al., 2001; Kenski et al., 2003). MARGA is a candidate for multi-pollutant monitoring in a future EPA monitoring network. The AiRRmonia employs a gas-permeable membrane that selectively passes NH_3 that is later detected by a calibrated conductivity cell. It was laboratory and field-tested in EPA's Environmental Technology Verification (ETV) program. Five other systems are based on spectroscopy or chemiluminescent detection principles. All have been tested in the ETV program; comprehensive reports on each one's performance are available. The last two monitors are research instruments: one detects ammonia via chemical ionization mass spectrometry (CIMS); the other uses a molybdenum oxide converter change N-containing species to NO and detects NH_3 through the chemiluminescent reaction of NO with ozone.

Other Type Samplers

A voltammetric microsensor for ammonia is under development at Argonne National Laboratories (Vogt and Skubal, 2005). Surrogate surfaces (smooth water surface and citric-acid coated paper on a knife-edge surface) are also described as a way to sample for NH_3 and NH_4^+. Analysis is by ion chromatography.

Sample Media Considerations

Passive samplers that use filters all specify citric acid treatment. Diffusion tube-type passive samplers specify a dilute solution of either hydrochloric acid or sulfuric acid as the absorbent media. The active denuder systems specify either a citric acid or phosphorous acid denuder surface coating to collect NH_3. Literature references report that phosphorus acid is preferred since it retains ammonium ion as ammonium phosphorate much more effectively than does ammonium citrate (McCulloch and Shendrikar, 2000). The CENRAP network uses phosphorous acid to coat denuders. Active samplers all use Teflon filters to entrain NH_4^+ containing particles for later analysis. Many also place a nylon filter downstream of the Teflon filter to catch volatile species arising from decomposition of NH_4NO_3 . The continual methods that employ denuders wet the denuder surface with aqueous solutions during use. The CENRAP manual denuder sampler uses the commonly accepted sampling media for NH_3 and NH_4^+.

Ammonia Monitoring Networks

In addition to the CENRAP Ammonia Monitoring Study and its predecessor network, the MRPO/CENRAP Midwest Ammonia Monitoring Study, our search located one network in Canada and five networks in Europe that monitor for gaseous ammonia. There are numerous other studies that measure ammonia gas but these are not listed since they were either short-duration special research studies (Super Sites) or projects that emphasized determination of ammonia emissions from sources such as poultry houses, CAFOs, or automobiles.

The CENRAP and Midwest RPO/CENRAP monitoring networks use the identical sampling and analysis methods. They collect a sample every sixth day and integrate the sample for 24 hours (Caughey and Gay, 2004). The United Kingdom National Monitoring Network and the Northern Ireland ammonia network both seek to determine if the ammonia emissions ceilings agreed upon for European countries are being exceeded and to follow concentration changes by determining long-term trends. These networks also are investigating seasonal and spatial patterns. The U.K. network uses a low-flow active NH_3 denuder/ NH_4^+ filter (DELTA system) that samples for a month in rural areas; the U.K. also employs a network of passive diffusion tubes to explore NH_3 variability in high concentration areas (Sutton et al., 2001; CEH, 2005). The Northern Ireland network uses the Adapted Low-cost Passive High Absorption (ALPHA) passive NH_3 sampler (Tang et al., 2004). It appears that sampling will continue for five to ten years in the U.K. and Northern Ireland. The biggest difference in the networks is the duration of the sampling: CENRAP integrates the air sample for 24 hours and takes measurements every six days; the U.K. and Northern Ireland networks integrate the air sample for a month (approximately 30 days or 720 hours).

The Swiss ammonia network operated for two years, October 1999 to September 2001. The Zürcher passive sampler was placed, in triplicate, at 41 sites; sample integration was from two weeks to one month. Emphasis was on estimating the annual mean and seasonal patterns of NH_3 and to compare to modeled annual concentrations. Activity-specific emission factors were developed, and models were used to map spatial emission patterns (Thöni et al. 2003; Thöni et al., 2004).

Two monitoring networks were used in the Netherlands. The most recent was a “dense” passive sampler network with monthly collections of samples at four agricultural areas operated from 1996 to 1999 (Duyzer et al., 2001). The data were compared to the OPS Lagrangian dispersion model outcome. The model underpredicted NH_3 by a factor of two. The second monitoring program is part of the Netherlands Air Quality Monitoring Network (Buijsman et al., 1998; Erisman et al., 2001). The reference reports its operation during the period 1992 to 1995; whether the network is still operating could not be determined. This eight-site network operated a multi-pollutant, continual monitor. The major problem with the monitor was high maintenance during the winter months.

The Canadian National Air Pollution Surveillance Network is most like the CENRAP network. It uses the R&P Partisol-Plus 2025 D sequential dichotomous sampler and the R&P Partisol Model 2300 PM2.5 speciation sampler (Dann, 2003). The six-site network began in 2000; it will eventually expand to 17 to 20 sites using methodologies similar to those used in the U.S.

EPA is considering establishing a 30- to 50-site multi-pollutant monitoring expansion of the CASTNET network that would include, among many other species, the continual (every 20 minutes to one hour resolution) analysis and electronic report of measurement of gaseous species such as SO_2, HNO_2, O_3, and possibly HNO_3 and NH_3, as well as sulfate, nitrate, and ammonium ion. The data would be available to the public within 24 hours of on-site analysis (Lear, 2005). The proposed sub-network is called National Core Monitoring Network (NCORE) Level 2. The continual sampler under evaluation is the MARGA sampler (see Table 1 for details), developed by the Energy Research Center for the Netherlands and Applikon, Inc. If 2005 field tests of this instrument and other continuous analyzers are successful, the samplers could be deployed for long-term evaluation in 2006. EPA is seeking partners to implement this planned network

Almost all of the NH_3 networks in the U.S., Canada, and Europe determine ammonia by one of three wet chemistry methods: colorimetry, ion chromatography, or conductivity measurements of NH_4^+ after selective passage of NH_3 through a semi-permeable membrane. The CENRAP specifically analyses using the Zellweger-Lachat Analytics, Inc., flow injection colorimetry system.

Conclusions

RTI’s evaluation of the research literature, emissions inventories, atmospheric modeling, monitoring networks internationally, and sampling and analysis techniques provided insight into the importance of ammonia in regional haze and the valuable role ambient ammonia monitoring can play in developing regional haze strategies. In the evaluation for CENRAP, RTI determined that CENRAP’s ambient ammonia monitoring network’s manual denuder, with particle collection on filters is recognized in most studies as the reference standard for intermittent monitoring. CENRAP collects a 24-hour integrated sample at seven sites every 6th calendar day. Upon evaluating more than 20 sampling/analysis techniques and their costs, RTI offered that day/night 12-hour sampling may be of interest; every 3rd day sampling would provide twice as much data and would match with Canada’s program. Passive sampler monitoring could be considered as a special study to better characterize source distribution and strength. As more and more manual methods are employed, the deployment of continuous methods becomes more attractive from cost and data completeness standpoints. It is important to ensure adequate meteorological data are available to support monitoring data. Finally, ammonium ion loss from the Teflon/nylon filter pack may be an issue that needs study.

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Using Ecosystem Models to Inventory and Mitigate Environmental Impacts of Agriculture

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Abstract

Agriculture is responsible for over 50% of global nitrous oxide (N_2O) emissions and is also an important source of nitric oxide (NO) and nitrogen dioxide (NO_2). N_2O is an important greenhouse gas (GHG) because it has a global warming potential ~300 times that of CO_2 and contributes to the destruction of stratospheric ozone (O_3). NO and NO_2, together known as NO_x, are precursors to surface level O_3 and contribute to nutrient loading of aquatic and terrestrial ecosystems. NO_x is also considered an indirect source of N_2O because after being emitted from agricultural soils it can be deposited on non-farm land, biochemically converted to N_2O, and emitted to the atmosphere. Field data show that N oxide emissions are primarily a function of soil texture, water content, N additions, and land management. These relations have been quantified and implemented in N oxide emission models. Soil disturbance (e.g. plowing) tends to decrease the proportion of NO_x compared to N_2O emissions and analyses have shown that the majority of agricultural NO_x emissions from agricultural soils in eastern Colorado are from rangeland as opposed to cropped soils. However, NO_x emissions from energy production, transportation, and industry are higher than agricultural emissions for most counties in eastern Colorado. The authors have developed a methodology to assess N oxide emissions from agricultural soils using empirical and process based models. This methodology has been used for the US inventory of GHG's and to evaluate different management strategies intended to mitigate environmental impacts of agriculture. US national maps of N oxide emissions from agricultural will be presented and the tradeoffs between N_2O and NO_x emissions and NO_3 leaching into waterways will be explored.

Introduction

Agriculture is responsible over half of anthropogenic N_2O emissions, a significant potion of NO_x emissions (~8%), and is a primary source of NO_3 leaching into waterways in the USA. Until recently, simple empirical models have been used to estimate these N loss vectors. However, the 2005 US Environmental Protection Agency greenhouse gas inventory estimates N_2O, NO_x, and NO_3 leaching losses by combining results from a process based model and empirical models (EPA, 2005). Empirical models are simple to use but N losses are based on N inputs and most of the other factors that control N losses are not included. Process-based models, on the other hand, account for N inputs as well as other factors (weather, soil class, timing and types of N inputs, cultivation events, land use history, etc.) that influence N losses. Another advantage of process-based models is they can be used to evaluate how different N loss mitigation strategies affect N losses, crop yields, soil carbon levels, and other ecosystem properties. We present results of county level simulations of major agricultural systems in the USA using the process-based biogeochemical model DAYCENT.

Methods

DAYCENT is the daily time step version of the CENTURY model. Major processes simulated include: plant growth and senescence, decomposition of litter and soil organic matter, N mineralization, nitrification, denitrification, and soil water/temperature fluxes (Parton et al., 1998, Del Gross et al., 2001). Model inputs are daily maximum/minimum air temperature and precipitation, vegetation type, soil texture class, and land management events. The ability of DAYCENT to reliably simulate crop yields, N_2O emissions, and NO_3 leaching has been validated by comparing model results with data representing different geographical regions, crop types, and land management practices (Del Grosso et al., 2005).

DAYCENT was used to estimate N losses for major crops and most grazed lands in the USA. The DAYCENT simulations of major crops (corn soybean, wheat, alfalfa hay, other hay, sorghum and cotton) and pastures accounted for ~86% and 75% of cropped and grazed land, respectively. For each crop in each county, DAYCENT outputs for N losses (in unit of gN m^{-2} $yr^{-1)}$ were multiplied by the NASS (http://www.nass.usda.gov/index.asp) reported crop area to obtain county level N losses for each crop. N losses for grazed lands in each county were calculated by multiplying DAYCENT outputs by grazing land area estimates derived from the National Resources Inventory (NRI, USDA, 2000). Then, losses for each crop and grazed land were summed to get total annual county level N losses for cropped /grazed systems.

Results and Discussion

Figure 1a shows DAYCENT simulated NO_x emissions and NO_3 leaching form cropped/grazed soils at the county level. Total county level N losses are mainly a function of N inputs, weather, soil texture, and the areas of cropped and grazed land in each county. NO_x emissions tend to be higher in the arid, western half of the USA. This is due to several reasons. DAYCENT assumes that NO_x losses are higher in grazed systems than cropped systems and grazed area is much greater in the western than the central or eastern USA. As soil gas diffusivity increases, NO_x from nitrification is more likely to be emitted from the soil surface before being reduced to N_2O or N_2. Drier soils have more air filled pore space than wetter soils so soil gas diffusivity tends to be higher in the arid west. Gas diffusivity also increases as soils become coarser textured. However, soils in some counties, e.g., the southeast USA, have low NO_x emissions even though they are coarse textured because the land area used for agriculture is small.

NO_3 leaching is high in the central USA where N inputs are high and rainfall events of sufficient magnitude to saturate the soil profile and leach NO_3 into the subsoil occur at sufficient frequency (Figure 1b). Leaching is also high in some western counties where irrigation is prevalent. We emphasize that in the arid west, the model is not simulating NO_3 leaching into ground or surface waters but leaching below the simulated soil profile and into the subsoil. That is, NO_3 can accumulate below the rooting zone in arid soils until a rainfall event of sufficient magnitude occurs to leach NO_3 from below the rooting zone and into the subsoil.

Conclusions

Agricultural soils are responsible for at least 50% of N_2O emissions and NO_3 leaching into waterways and a small but significant portion of NO_x emissions in the USA. N inputs, weather, soil type, and land management interact to control these N loss vectors. Process-based models that account for these interactions should yield more reliable estimates of these losses than simple empirical models. The process-based model DAYCENT has simulated N_2O, NO_x, and NO_3 losses for agricultural soils in the USA at county level resolution for current land management practices. DAYCENT has also been used to compare different mitigation strategies. Simulations suggest that use of nitrification inhibitors and precision application of N fertilizers can decrease N gas losses and NO_3 leaching while maintaining or increasing crop yields. Simulations also suggest that conversion to no till cultivation can sequester C in soil, but that in some systems, no till can lead to higher N gas and N leaching losses than conventional plowing. Therefore, the impacts of different land management practices on greenhouse gas fluxes and NOx emissions and NO_3 leaching must all be considered when deciding overall best management strategies for different regions in the USA.

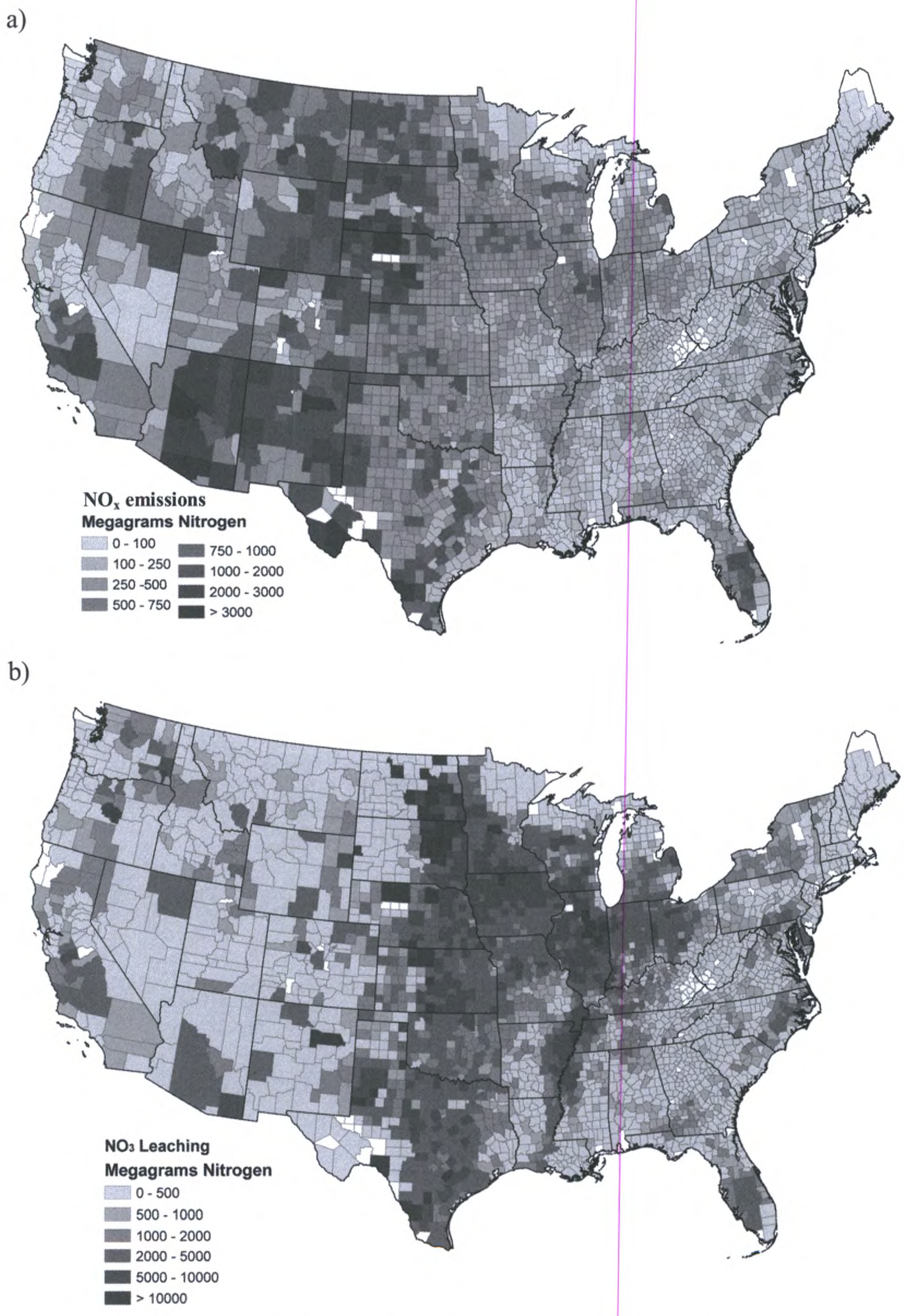

Figure 1. DAYCENT Simulated county level NO$_x$ emission (a) and NO$_3$ leaching (b) for cropped/grazed lands in the USA

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Impacts of Acid Sulfate Soils on Air Quality

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Abstract

Many coastal lowland soils were deposited under marine conditions and contain large amounts of sulfides, principally as pyrite. When these soils, referred to as acid sulfate soils (ASS), are drained for development, the sulfides oxidize with the production of acidic ground water that can pose severe environmental problems. Typically, Australian coastal ASS have high organic carbon contents and high porosities in the surface soil, high water tables and low pH. These characteristics, their use for intensive sugarcane production, and their location in warm, moist climate zones suggest that they could be large emitters of S gases such as SO_2, an indirect greenhouse gas, and the direct greenhouse gases CO_2, N_2O and CH_4. The paper reports a study in which emissions of these gases from an Australian ASS producing sugarcane were measured with micrometeorological techniques. We found substantial emissions of SO_2, averaging 21±15 ngS m^{-2} s^{-1}. Including these in our data base for 7 years of measurement, we estimate a global source of S from ASS amounting to 2 to 3% of known anthropogenic emissions of S. Our data base for the direct greenhouse gases is smaller, but in this study, CO_2 emissions averaged 0.25±0.04 mg m^{-2} s^{-1}, which is in the top of the range for agricultural soils, and N_2O emissions averaged 70±22 ngN m^{-2} s^{-1} over 22 days, which is several times larger than emissions usually reported for agricultural soils. Results for CH_4 are equivocal: micrometeorological measurements suggest emissions are non-trivial, but the measured fluxes are near our limits of detection. A bigger data base is needed. Both soil moisture and soil temperature appear to be important drivers of gas emissions.

Introduction

Many Holocene sediments in coastal lowlands were deposited under marine conditions and the soils that were formed contained large amounts of sulfides, principally as pyrite (iron sulfide). When these soils are drained for agriculture or commercial developments, the sulfides oxidise and produce a range of dissolved sulfur species in highly acidic ground water. These soils are often referred to as acid sulfate soils (ASS). Andriesse and Mensvoort (2003) estimate that there are around 17 million ha of such soils in the world, but Dent (1986) suggests that they may occupy > 100 million ha, while White et al. (1996) suggest 200 million ha and estimate that there are 4 million ha of ASS in Australia. Large areas occur also in Asia, Africa and Latin America. Typically, ASS have high organic carbon contents and high porosity in the surface soil, high water tables and low pH. The high sulfur (S) content suggests that they could emit S gases such as sulfur dioxide (SO_2), an indirect greenhouse gas, while the high soil moisture regimes, high soil temperatures and high levels of available carbon resulting from trash retention that characterise Australian sugarcane culture, where our work has been conducted, have all been shown to be conducive to elevated emissions of the greenhouse gases methane (CH_4) and nitrous oxide (N_2O) and to have a substantial influence on carbon dioxide (CO_2) exchange and carbon sequestering. We report preliminary results from a program to quantify emissions of these gases from fallow acid sulfate soils cultivated for sugarcane production in the valley of the Tweed River in northern NSW, Australia. The program aims to measure emissions on a year-round basis, using both chamber and micrometeorological techniques. Here, we report on one series of continuous emission measurements made in the early summer using a micrometeorological approach.

The Gases

SO_2

Sulfur dioxide in the atmosphere leads to aerosol formation, acid rain and greenhouse effects through influences of aerosols on the earth's radiation balance. Soils have long been recognised as SO_2 sinks (Garland 1977), but Macdonald et al. (2004) showed unequivocally that SO_2 can be emitted from ASS and that its emission appears to be coupled to the evaporation of soil water containing sulfite. In the present paper we confirm those initial findings of Macdonald et al. (2004) with continuous micrometeorological measurements extending over several days and soil moisture states. The new data have allowed us to refine the previous estimates of global emissions of SO_2 from this source.

CO_2

The high organic C content of the soils under study and the addition of C residues from sugarcane production, together with high soil moisture contents and high soil temperatures, might be expected to favour high CO_2 production rates. On the other hand, the model of Vallis et al. (1996) predicts that the same factors could also be expected to promote higher carbon sequestration in soils. Little experimental work has been done on this topic.

N_2O

Soil nitrogen (N) undergoes a number of transformations that lead to the formation of N_2O, a greenhouse gas with a high global warming potential. Weier et al. (1996) used chamber techniques to study N_2O losses from soils used for sugarcane production in Australia. Based on that work, Weier (1998) estimated that Australian sugarcane soils emit 10 kT N_2O-N ha^{-1} y^{-1}, which is about 1/3 of the estimated N_2O emissions from all agricultural soils in the country, and found that emissions from the ASS he studied were the highest of all.

CH_4

Typically, the surface horizon of the ASS we have worked with has a high organic C content of 15% and a porosity of 60%, while a water table exists at depths between 0.2 and 0.5 m. The soils are often inundated. These are conditions highly conducive to CH_4 formation. We are not aware of any previous reports of measurements of CH_4 emissions from ASS on a field scale.

Methods

Site

Measurements were made on a fallow field used for sugarcane production in the valley of the Tweed River, northern NSW (28°18'S, 153°31'E) in Eastern Australia. The surface soil is an organic clay loam with a high porosity, near 0.6, and an organic carbon content of 15%. The subsoil is 85% clay and a water table exists at 0.2 to 0.5m. The acidic A2 horizon is formed from the oxidation of pyrite; 50 t/ha of sulfuric acid can occur within this horizon. Soil pH values are < 4.0. The climate is humid and subtropical with summer-dominant average rainfall of 1585 mm. Falls of rain are frequent. The study was made in the early summer of 2003, between November 27 and December 14. It was interrupted half-way by a rainfall of 63mm.

Micrometeorological Flux Measurement

We employed a flux-gradient micrometeorological technique, outlined by Denmead (1994). Rates of gas emission, F_g, were calculated as the product of an atmospheric transfer coefficient, h, derived from statistics of the wind and atmospheric stability, and the difference in the atmospheric concentrations of gas, C_i, between two heights above the surface, z_1 and z_2:

$$F_g = h(C_1 - C_2)\,. \qquad [1]$$

The relevant measurements were made in a large, fallow field with a minimum fetch of 150m. The measurement heights were set at 0.5m and 1.5m.

Concentrations of SO_2 were measured with a UV pulsed-fluorescence SO_2 analyser (Monitor Labs Model 9850) mounted in the field in a thermally insulated enclosure. Air from each of the 2 intake heights was drawn into the analyser through 5m of Teflon tubing. The sampling sequence was to switch between intakes every 15 min, allow 3 min for equilibration to the new air-stream, and then measure every 10s for 12 min. The data were averaged to yield C_1 and C_2 for each 30-min run. Concentrations of the direct greenhouse gases were measured with an FTIR spectrometer which measures, simultaneously, the concentrations of CO_2, N_2O and CH_4 in the air stream (Griffith et al., 2002). The sampling scheme was similar to that employed for SO_2, but the air streams were drawn 100 to 200m to an air-conditioned trailer housing the spectrometer.

Gas concentrations and micrometerorological parameters needed to calculate *h* were measured at the centres of the experimental fields. The measurements included fluxes of heat, water vapour, and momentum, calculated from differences in temperature, humidity and wind speed between the two measuring heights, gas concentraions at the two measuring heights, net radiation, soil heat flux, soil temperatures, soil moisture contents and wind direction. Mean values of *h* were calculated for successive 30-min runs.

Results and Discussion

We use ensemble means to illustrate the magnitudes and diurnal variation of weather variables and fluxes during the study, and we have calculated these separately for the 7 days before the rainfall of 63 mm on December 5 and 6 and the 7 days afterwards. The ensemble averages are the means of all measurements made at the same time of day. Presentation of the data in this way allows consistent diurnal trends to be observed and provides a measure of day to day variation through the standard errors of the ensemble means.

Soil evaporation and Soil Temperature

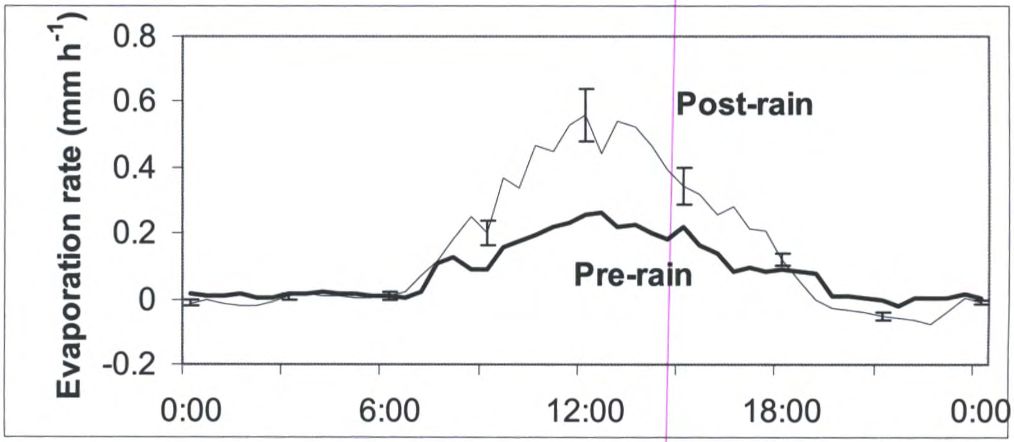

Figure 1. Ensemble evaporation rates for 7 days before and 7 days after a rainfall of 63mm. The error bars are representative standard errors of the means.

The ensemble evaporation rates and soil temperatures for the pre- and post-rain periods are shown in Figs. 1 and 2. The average evaporation rate almost doubled while the average soil temperature decreased by 8°C after the rain. These changes were indicative of the moisture status of the soil, which had a large influence on gas emissions.

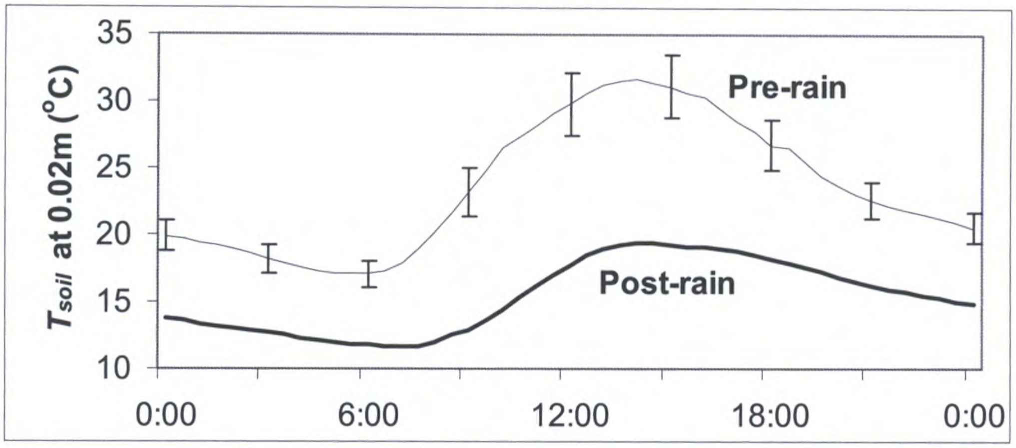

Figure 2. Ensemble soil temperatures for the pre- and post-rain periods. Error bars as in Fig. 1.

SO_2 emissions

The diurnal variation and the magnitudes of emissions of SO_2 can be seen in Fig. 3 which shows ensemble averages of the SO_2 flux. There was a marked diurnal cycle in emission rate with maximum rates around noon and virtually no emission over night. The time course of the emissions was similar to that of evaporation, confirming the coupling between the two processes that we observed in our earlier studies (Macdonald et al., 2004). However, the time course for SO_2 emission was rather different from that of soil temperature. The latter exhibited a slow decline overnight, whereas SO_2 emission virtually ceased early in the evening. Another factor contributing to the diurnal variation in emission rates for this and the other gases examined could well be the day-night variation in the water-filled pore space (WFPS) of the surface soil caused by evaporation of water by day and recharge overnight. The differences in WFPS that occurred between day and night corresponded roughly to a 2 to 1 difference in the air-filled pore space of the surface soil, which would have a significant influence on the effective gas diffusion coefficients.

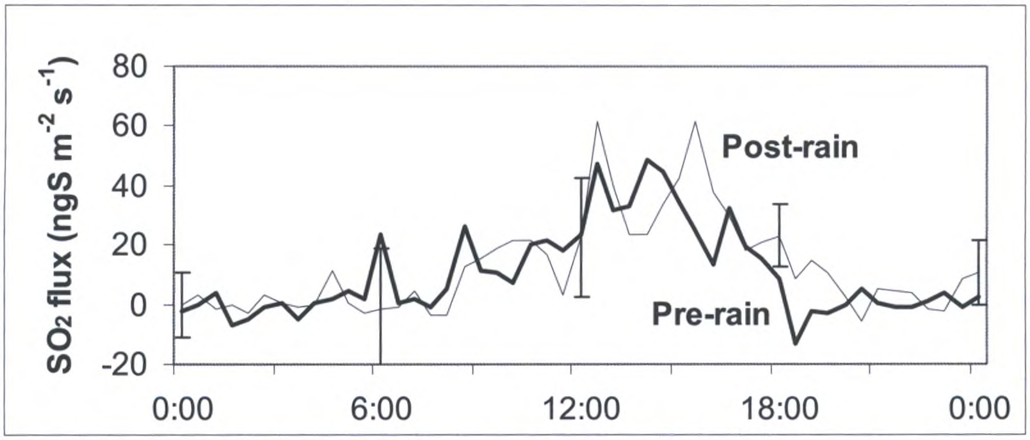

Figure 3. Ensemble means of SO_2 emission rates in pre-and post-rain periods. Error bars as in Fig. 1.

Interestingly, there was no significant difference between emission rates before and after the rain. However, comparison with other years suggests that both evaporation rate and soil temperaure influence the rate of SO_2 emission. It may be that the lower soil temperatures after the rain hindered SO_2 production. It may be also that the higher soil water contents after the rain tended to keep the SO_2 in solution. Macdonald et al. (2004) suggest that SO_2 emission is more likely to occur from drying soils than from those that are too wet or too dry. The rates of emission in Fig.3 are comparable with those we have measured in other years. They are discussed further in a later section.

CO_2 emissions

Ensemble means are shown in Fig.4. The time-courses seemed to follow that of soil temperature (cf. Fig. 2), although the loss of some data means that there were not enough observations to define the diurnal cycle precisely In this case, there was a marked increase in gas production after the rain. The mean 24-h emission rate over the whole sampling period period was 0.25±0.04 mg m^{-2} s^{-1}.

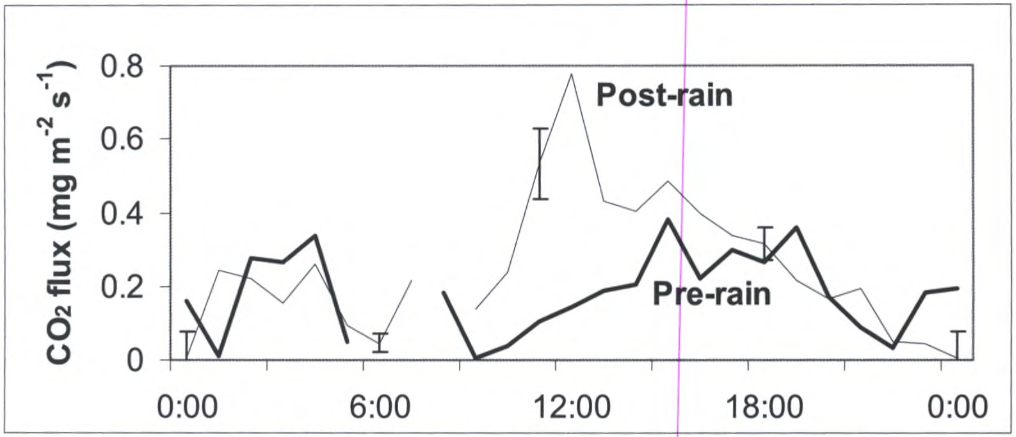

Figure 4. Ensemble means of CO_2 emission rate. Error bars as in Fig. 1.

N_2O Emissions

Figure 5 shows the time courses of N_2O emissions before and after the rain. A clear diurnal cycle was evident in both periods with maximum emission rates by day and minimum rates by night. The time courses of N_2O emission tended to follow that of T_{soil}, exhibiting maxima in the afternoon and a slow decline through the afternoon and evening. N_2O emissions are reported to have a Q_{10} (relative change in emission rate for a 10°C change in temperature) of 2 or more (Davidson and Schimel, 1995).

Nitrous oxide production is known to increase with WFPS up to a WFPS of 80 or 90% (Davidson and Schimel, 1995). In the present study, the mean WFPS was around 30% in the period before the rain and around 50% after it. As expected, N_2O emission increased markedly in the latter period; it more than doubled.

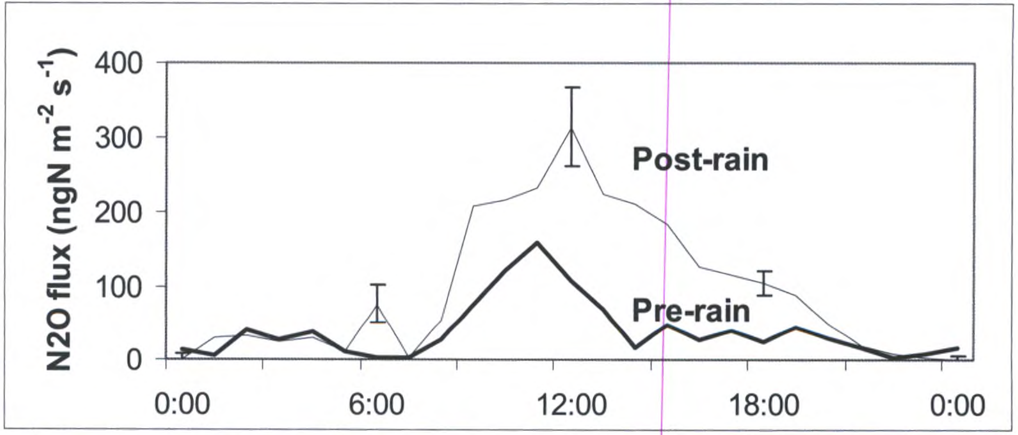

Figure 5. Ensemble means of N_2O emission rate. Error bars as in Fig. 1

CH_4 emissions

Diurnal cycles similar to those for N_2O were observed for CH_4. However, we have less confidence in these measurements because of the difficulty in measuring the small CH_4 concentration gradients. The resolution of the FTIR system is about 0.1% of the gas concentration (Griffith et al., 2002). Applying this figure to a background concentration of 1800 ppb for CH_4 and assuming typical transfer coefficients of 0.1 m s^{-1} for the day-time and 0.02 m s^{-1} for night-time, leads (via Equation 1) to lower limits of flux detection of around 200 ng m^{-2} s^{-1} by day and 50 ng m^{-2} s^{-1} by night. Many of the fluxes we have measured are close to these limits; the mean 24-h emission rate over the measurement period was 180±40 ng m^{-2} s^{-1}. However, the apparent existence of a diurnal cycle suggests that emissions were occurring.

Comparisons

The measured emision rates for the various gases are compared with those from other soils below. .

SO_2

Our earlier estimate of the global emissions of SO_2 from ASS (Macdonald et al., 2004) was based on a "typical" emision rate of 31 ngS m^{-2} s^{-1} and a global area of ASS of 200 million ha. Including the present results in the data base reduces the overall mean to 21±15 ngS m^{-2} s^{-1}, which is about 2/3 of the previous figure. Our estimate of the annual global source of S from ASS becomes 1.3 TgS, compared with our previous estimate of 2 TgS. The new rate still supports the contention of Macdonald et al. (2004) that emissions of S to the atmosphere from ASS are at least of the same magnitude as the total emission of S from terrestrial biogenic sources identified to date, or those from biomass burning. They are around 2% of currently recognised anthropogenic emissions of S (Bates et al., 1992). Whether SO_2 emissions from ASS are anthropogenic is arguable. It is recognised that these soils can result from natural pedogenesis, and so can be natural sources of SO_2. We believe, however, that SO_2 production is probably increased by anthropogenic disturbance.

CO_2

The data base is small and no concrete conclusions can be reached. The mean emission rate during the present study was 0.25±0.04 mg m^{-2} s^{-1}. This rate appears to be at the top of the range commonly reported for CO_2 emissions from agricultural soils (0.06 to 0.10 mg m^{-2} s^{-1}), e.g., Weier (1998) and Wagner-Riddle et al. (1997).

N_2O

The mean emission rate for the present study was 70±22 ngN m^{-2} s^{-1}. This rate is substantial in comparison with those reported for other soils. Wagner-Riddle et al. (1997), for instance, measured emission rates for N_2O in various cropping sequences in Canada that were between 19 and 39 ngN m^{-2} s^{-1}, Laville et al. (1997) measured emisions of just 6 ngN m^{-2} s^{-1} from bare soils after the addition of 150 kgN ha^{-1} of N fertiliser, and Phillips et al. (2006) measured annual emissions of N_2O from irrigated, fertilised, grazed pastures corresponding to only 11 ngN m^{-2} s^{-1} although the annual inputs of N were 875 kgN ha^{-1} (225 from fertiliser and 650 from urine and faeces). The emissions measured by us, however, are of the same magnitude as those measured by Weier et al. (1996) on a similar ASS. It appears that the potential for emissions of N_2O from cultivated ASS is high.

CH_4

We do not yet have enough reliable data to reach solid conclusions. The mean emission rate for the micrometeorological measurements we have made was 140 ng m^{-2} s^{-1}. This last rate is 2 to 10% of CH_4 emission rates observed for wetlands and rice paddies (Wassman et al., 2000; Bartlett et al., 1988). If this proves to be a consistent result, it would suggest that ASS are non-trivial sources of atmospheric CH_4. More data are needed. As for SO_2, we do not know whether CH_4 emissions from ASS should be classified as natural or anthropogenic.

Summary and Conclusions

There was a marked diurnal cycle in the emission patterns of all the greenhouse gases. This points to the need for continuous measurement systems and the difficulty of extrapolating from one or a few emission measurements per day to a 24-h total.

Our data base is small, but the ASS which we have studied appear to be potentially rich sources of direct and indirect greenhouse gases. We can note particularly that:

- The additional measurements of SO_2 emission presented here confirm our earlier contention that ASS are non-trivial sources of atmospheric SO_2. We estimate an annual global emision between 1 and 2 TgS, which is 2 to 3% of all anthropogenic emissions.
- Emissions of CO_2 from the soil are at the upper end of those measured previously for sugarcane and other agricultural soils.
- The emissions of N_2O that we have measured are 2 to 10 times higher than those measured for other N-fertilised soils.
- Better resolution is needed for gradient measurements of the CH_4 flux.

Acknowledgements

We acknowledge the financial support of the Australian Research Council, the Tweed Shire Council and the Australian Greenhouse Office. We thank Robert Quirk and Bill Stainlay, on whose farms the work was done, for their co-operation and encouragement. Special thanks are due Mira Durr for assistance in the field.

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Micrometeorological Methods for Estimating Surface Fluxes from Geologically Stored CO_2 at Scales 1 - 1000 m.

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Abstract

Geosequestration is the storage of CO_2 in geological formations after its capture from industrial sources such as coal-fired electric power stations and from oil and natural gas fields. Geosequestration offers a potentially effective greenhouse gas control measure by withholding CO_2 from the atmosphere for centuries to millennia. This poster outlines how emissions of CO_2 to the atmosphere during injection and following geological storage might be detected, attributed to a source and quantified, in an environment where CO_2 is ubiquitous and highly variable. A three step strategy is identified to monitor leakages from geologically stored CO_2 using atmospheric measurements: 1) Detection of sources and measurement of CO_2 concentrations to comply with environmental health and safety requirements. 2) Attribution of leakages associated with geosequestration and distinguishing them from biogenic and industrial sources. 3) Quantification of the leakage rates from identified geosequestration sources. Various methods to monitor continuously emissions of CO_2 from land surfaces at spatial scales from 1 - 1000 m are presented. Once source areas are identified, static or dynamic chambers placed on the surface are suitable for measuring small fluxes from small areas but significant replication is needed because of often large spatial variability in emissions. Micrometeorological mass-balance, eddy covariance and flux-profile methods integrate over larger areas but require high-precision instruments to measure small concentration gradients. Eddy covariance and flux-profile approaches are appropriate when the sources are uniform over large areas (upwind fetch to measuring height > 100) and the fluxes are one-dimensional. Mass balance techniques calculate emissions by measuring flux divergences through the walls of a control volume in the atmosphere and are suitable for estimating fluxes from areas up to 100 x 100 m^2. Backward Lagrangian dispersion analysis and atmospheric tracer techniques are suitable for point, line and area sources of known dimensions from 1 to 100 m. All techniques need to distinguish between emissions from geosequestration and biological sources and sinks, examples of which are presented.

Variations in Particle Composition and Size Distributions in and around a Deep Pit Swine Operation

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Abstract

Agricultural facilities are the source of many types of particles and gases that can exhibit an influence on air quality. Emissions potentially impacting air quality from agricultural sources have become a concern for regulatory agencies such as the United States Department of Agriculture (USDA) and the Environmental Protection Agency (EPA). Particle mass concentration influences from agricultural sources can include both primary particles (direct emissions such as dust) and secondary particles (formed from gaseous precursors such as ammonia).

In support of other investigations at a swine production facility (Zavylov, 2006), continuous and near real-time measurements of particulate size distribution and composition were obtained. The facility consisted of three separate, parallel, deep-pit style barns. Each barn housed around 1,250 pigs with an average weight of approximately 90 pounds per animal. A single trailer was equipped with an aerosol mass spectrometer (AMS-Aerodyne, Inc.), a $PM_{2.5}$ elemental/organic carbon (EC/OC) analyzer (R&P, Inc., Series 5400) and an eight-stage cascade impactor (Tisch Environmental, Inc., Model TE-20-800). The trailer was located approximately 40 meters north (downwind based on available historic data) of the nearest barn. This suite of instrumentation allowed characterization of a wide range of particulate properties.

The aerosol mass spectrometer provides real-time information on particle size and chemistry. The AMS analyzed particles in the size range of ~30 nm to ~1 μm. Throughout the study, the AMS detected mass concentrations in this size range of 3-5 $\mu g\ m^{-3}$. The AMS consistently observed organic carbon as the dominant particulate constituent within this size range, with OC making up ~60% of the total mass during a typical time period. Smaller amounts of sulfate and nitrate were detected.

The real-time carbon analyzer found typical out-of-plume elemental and organic $PM_{2.5}$ carbon concentrations on the order of 0.4 and 1.2 $\mu g\ m^{-3}$, respectively. In-plume concentrations were observed with nominal values of 2.2 and 4.0 $\mu g\ m^{-3}$, respectively. These mass concentrations are consistent with the values reported by AMS.

Several optical particle counters (MetOne, Inc. Model 9012) and portable PM_{10}/$PM_{2.5}$ samplers (AirMetrics MiniVol) were arrayed (collocated) within and around the facility in order to determine particle plume transport throughout the facility. Background PM_{10} and $PM_{2.5}$ concentrations were found to average around 35 and 10 $\mu g\ m^{-3}$, respectively. In-plume values were 40-60 and 10-15 $\mu g\ m^{-3}$, respectively, depending on sampler location relative to the barns. The eight channel optical particle counters remotely recorded real-time number concentration data over particle size ranges from 0.3 μm to 10 μm and showed size distribution variations as a function of time and sampler location. Of special note were the differences observed for the horizontally-collocated but vertically-separated samplers, which indicated the facility's plume was emitted straight aloft directly above the building.

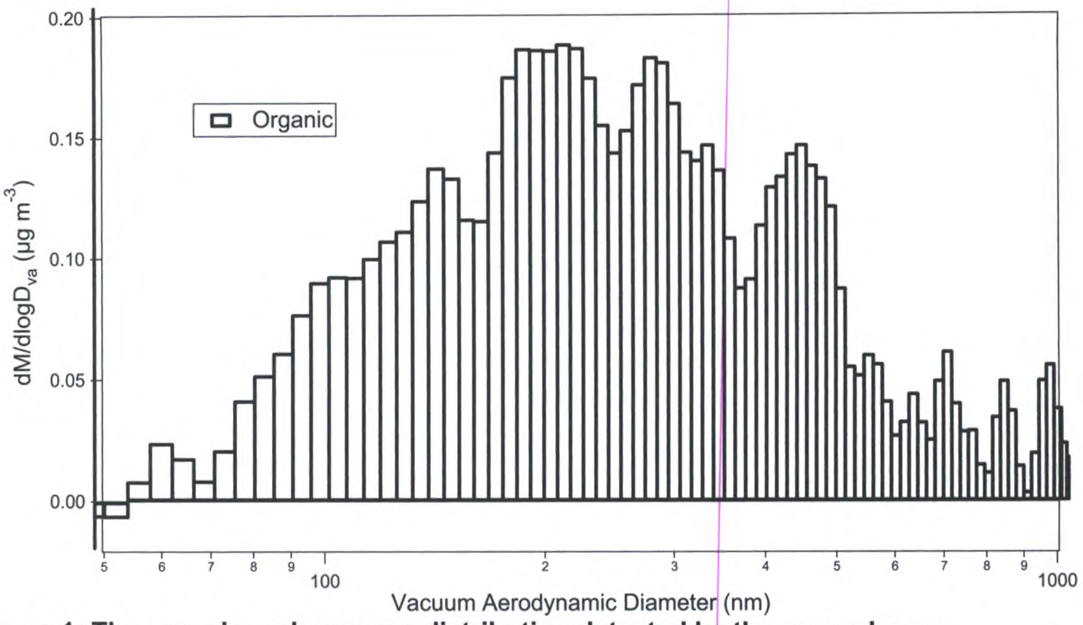

Figure 1: The organic carbon mass distribution detected by the aerosol mass spectrometer (eight hour average) at a pig barn facility in Ames, Iowa, 30 August 2005.

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Comparison of Dispersion Models for Ammonia Emissions from a Ground Level Area Source

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Abstract

Dispersion models are used determining and regulating pollutant emissions from many sources, including ground level area sources such as feedlots, dairies, and agricultural field operations. The most commonly used EPA approved dispersion model is Industrial Source Complex Short Term Version 3 (ISCST3), but as of November 2006, AERMOD-PRIME will be replacing ISCST3 as the EPA approved model. Therefore, emission factors that have been used with ISCST3 to determine compliance with air quality regulations will now be used in conjunction with AERMOD-PRIME. This study compares the emission fluxes of ammonia from a feedlot in the Texas panhandle determined using four dispersion models: ISCST3, AERMOD-PRIME, WindTrax®, and AUSTAL. ISCST3 and AERMOD are Gaussian plume models, while WindTrax® and AUSTAL are backward and forward Lagrangian Stochastic models, respectively. Identical downwind ammonia concentration data was entered into each model as well as three different meteorological databases. The results of this study indicate that Lagrangian Stochastic and backward Lagrangian Stochastic models result in higher modeled fluxes. Furthermore, AERMOD is less conservative than ISCST3. These results indicate that calculated emission rates and/or emission factors are model specific, and no simple conversion factor can be used to adjust factors between models. Therefore, emission factors developed using one model should not be used in other models to determine downwind pollutant concentrations.

Monitoring Odour Abatement Technology by Means of Membrane Inlet Mass Spectrometry (MIMS)

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Abstract

A chemical measurement of odour compounds has the potential to provide accurate assessment of odour and odour reduction if the major odour compounds are known. Membrane Inlet Mass Spectrometry (MIMS) is a chemical measurement technique capable of detecting a range of volatile compounds, including odour compounds. MIMS detects organic compounds directly without any sample preparation by passing a stream of air by a thin silicone membrane placed in front of a quadrupole mass spectrometer. Volatile organic compounds diffuse into the membrane and are transported into the mass spectrometer due to the vacuum conditions. The direct sampling makes MIMS suitable for field on-line measurements, and MIMS is therefore particularly useful for optimization procedures where a fast response is highly advantageous. MIMS can also be used for long-term monitoring, e.g. for documenting the stability of a certain odour abatement process.

Since MIMS detects all volatile compounds entering the mass spectrometer without chromatographic separation, there is a potential risk for cross-compound interferences. In practice, however, it is shown that the MS signals can be assigned to groups of structurally related compounds, e.g. volatile fatty acids and reduced sulphur compounds, if not to individual compounds.

Introduction

Odour nuisance is an increasing problem for the local population in many areas due to intensified livestock production. In order to maintain a cost-effective agricultural production in accordance with the local society, there is therefore a need for efficient odour abatement technologies. A number of technologies are proposed, developed and implemented, e.g. biofilters and chemical scrubbers. Testing, evaluating and optimizing such technologies require reliable and accurate methodologies for measuring odour and the efficiencies of odour abatement technologies. Traditionally, the efficiency of odour reduction has been measured by olfactometry based on the odour perception of a trained human panel. Olfactometry is of relevance because it is a direct measure of the actual physiological effect of odour mixtures. However, it is generally accepted that there is substantial uncertainty associated with the measurements. This is particularly a disadvantage in relation to technology optimization where small improvements thus cannot be identified with certainty.

Chemical measurements of odour compounds can in principle be carried out with great accuracy. Provided that the major odour compounds can be identified and the relationship between odour compounds and odour perception can be established with a reasonable statistical certainty, chemical measurements therefore has the potential to supplement and partly replace olfactometry.

Measurements based on gas chromatography with mass spectrometric detection (GC/MS) has been used to detect and identify odour compounds from manure and livestock facilities (Blunden et al., 2005; Hobbs et al., 1998; Schiffman et al., 2001).

Here, we present a related technique, membrane inlet mass spectrometry (MIMS) (Ketola et al., 1997; Ketola et al., 2002). Compared to GC/MS, MIMS is a direct measurement technique, which allows for on-line measurements of odour compounds. Examples of measurements include monitoring the efficiency of biofilters and the effect of cooling ventilation air.

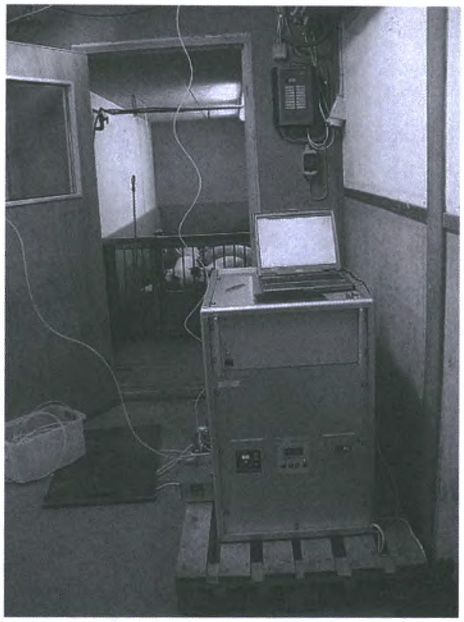

Figure 1. MIMS-instrument in a pig stable

Methods

A mass spectrometer (Balzers, QMG 420) equipped with a membrane inlet consisting of a temperature controlled membrane (50 µm polydimethyl siloxane) and a stainless steel air intake was used for the measurements presented in this paper. An air pump was used to pass unfiltered air by the membrane at a flow rate of ~200 ml/min providing turbulent conditions near the membrane surface, which gives the most efficient uptake of volatile compounds. Odour compounds are sampled from the air by absorption into the membrane, and because of the low pressure inside the mass spectrometer compounds diffuse through the membrane and evaporate into the ion source of the mass spectrometer.

In order to monitor the efficiency of odour abatement technologies, a multiposition valve was used to multiplex between air influenced by the technology, reference air and background (clean) air. In case of a biofilter, for example, a measurement cycle consists of 1) clean air, 2) air sampled before the filter and 3) air sampled after the filter. The efficiency with respect to a certain compound is estimated from the background-subtracted signals before and after the filter, respectively.

Results and Discussion

Basic Studies of MIMS Response to Odour Compounds

In Figure 2, a mass spectrum obtained by sampling the headspace of manure from a Danish pig farm is presented. The sample represents a concentrated odour sample compared to typical emission levels from pig farms and is useful for evaluating which compounds contribute to the main MIMS-signals.

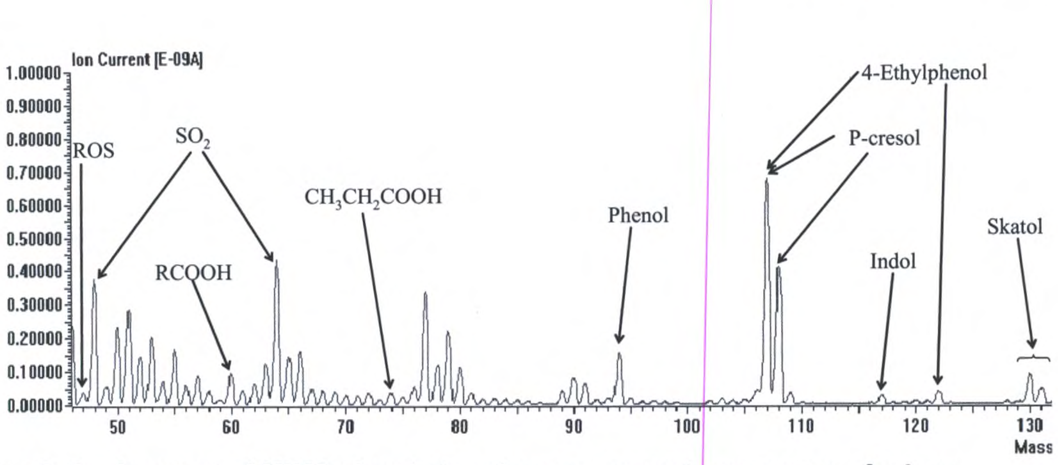

Figure 2. Assignment of MIMS-signals to odour compounds or groups of odour compounds. The x-axis is the mass/charge ratio (m/z) of the ions formed.

It can be seen from Figure 2, that several of the major MIMS-signals can be assigned to important odour compounds or structurally related groups of compounds. Some signals, e.g. from m/z 50 – 58 and from m/z 77 – 80 are less specific and therefore less useful for monitoring odour compounds. The composition of the sample was confirmed by GC/MS.

There are a number of carboxylic acids present in typical samples from pig facilities. These give rise to overlapping MIMS-signals at m/z 60, 73 and 74. Therefore carboxylic acids are mainly measured as groups of compounds according to these signals. Likewise, reduced organic sulphur compounds are detected by a common signal at m/z 47 corresponding to compounds containing the CH_3S- moiety, which mainly comprise methyl mercaptan, dimethyl sulphide and dimethyl disulphide. These sulphur compounds give rise to other MS-fragments that are not, however, unambiguous due to overlapping with other compounds. Other odour compounds, like skatol and indol, possess more specific MS signals.

The sensitivity of MIMS is compound specific and is related to the volatility and polarity of the compound and hence its ability to be absorbed into the non-polar membrane. Carboxylic acids, for example, are highly abundant (as quantified by GC/MS) but do not give rise to the largest MIMS signals due to their high polarity.

An important feature of MIMS is the linearity of the response as a function of concentration. In Figure 3, examples of calibration curves for carboxylic acids (RCOOH; the sum of carboxylic acids containing the mass spectrometric fragment with m/z 60) and p-cresol (4-methylphenol) are shown. The data in Figure 3 was obtained by injecting various amounts of a synthetic mixture of 10 important odour compounds into a Tedlar sampling bag and analyzing by MIMS. The concentration levels were selected in order to cover real-world concentration levels.

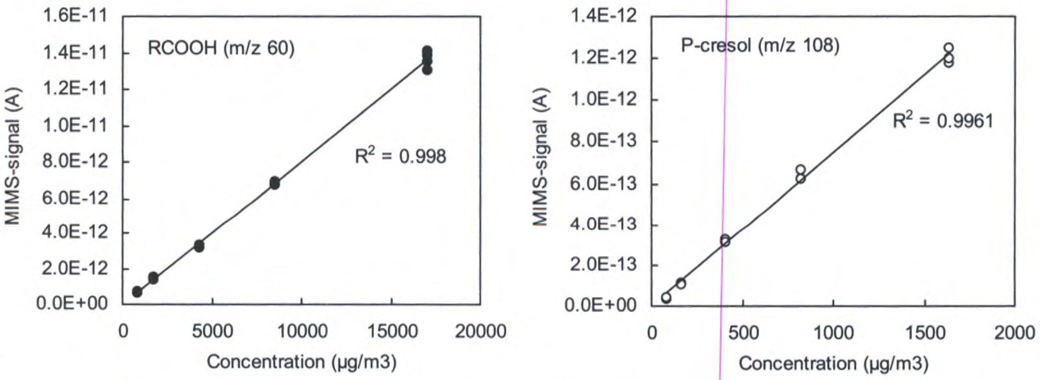

Figure 3. Calibration curves of RCOOH (carboxylic acids) and p-cresol. The straight curves are linear regression data.

Application of MIMS for Monitoring Odour Reduction

An example of results from the application of MIMS for monitoring the efficiency of a biofilter is presented in Figure 4. It appears that the efficiency of the filter towards different compounds is quite stable, whereas there is more variation regarding the efficiency towards different types of compounds. P-cresol and carboxylic acids are efficiently removed, whereas organic sulphur compounds are less reduced and with much more variability in the results. These results are not surprising since it is a prerequisite for efficient removal that the odour compounds are absorbed into the aqueous phase of the biofilter. Organic sulphur compounds, such as dimethyl sulphide, are much less water soluble than carboxylic acids or p-cresol.

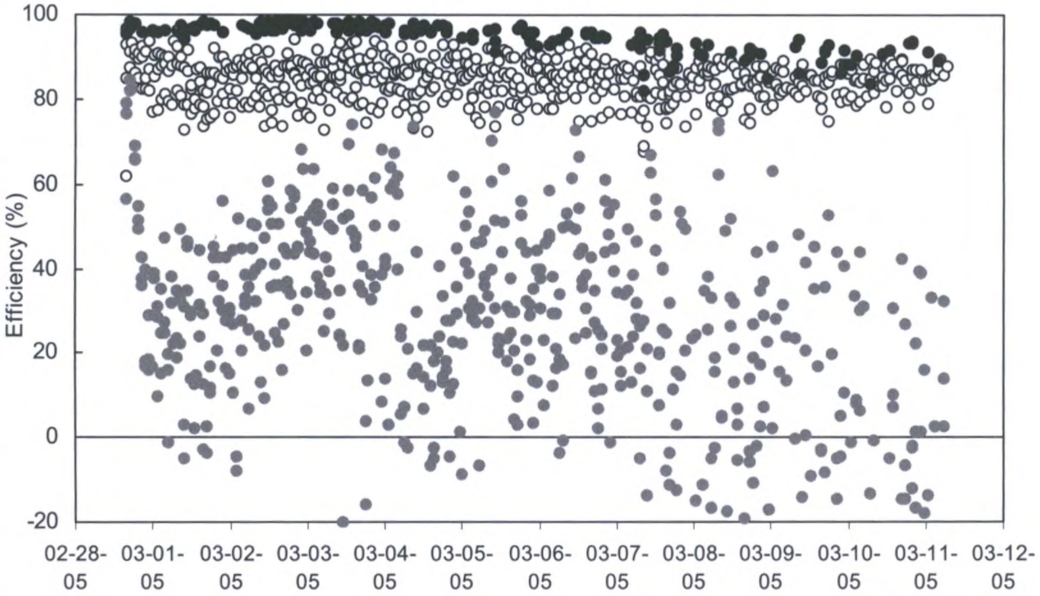

Figure 4. Biofilter efficiencies towards p-cresol (black circles), RCOOH (open circles) and reduced organic sulphur compounds (ROS; grey circles). Data from March 2005. The efficiency is estimated from the MIMS signals before and after the filter.

Another example of application of MIMS is presented in Figure 5. In this case, the effect of cooling ventilation air on odour emission was investigated. Two pig stable sections were compared. In one section, the intake ventilation air was cooled in order to reduce the ventilation rate to about 50 %, whereas the other section had a normal ventilation rate. In Figure 5, the relative effect of cooling on the emissions of carboxylic acids and p-cresol are presented as the average diurnal variation of the measurement period of four days. A relative effect of <1 corresponds to a reduction in the emission caused by cooling.

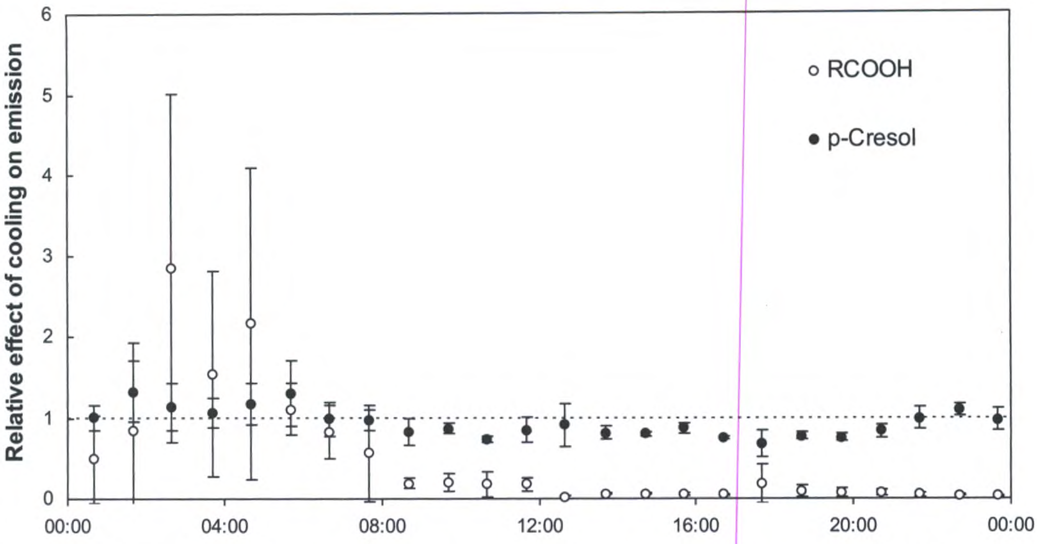

Figure 5. Average diurnal variation of the relative effect of cooling ventilation air on the emissions of carboxylic acids (RCOOH) and p-cresol. A relative effect of <1 corresponds to a reduction caused by cooling. Error bars represent the variation in the data.

The effect of cooling on p-cresol is relatively small with a small reduction during daytime and small increase during nighttime in the section with cooling. Contrary to this, emission of carboxylic acids was significantly reduced during daytime and evening, but was more strongly increased during nighttime, although the variability in the data is quite large. The mechanisms behind these patterns cannot be elucidated from the current work, but the results demonstrate the ability of continuous measurements to demonstrate temporal variations that cannot be observed from single samples for olfactometric analysis or laboratory chemical analysis.

Comparison with Olfactometry

A dataset consisting of olfactometric measurements and MIMS-measurements were subject to multivariate statistical analysis in order to attempt to elucidate a statistical relationship between odour reduction observed by olfactometry and odour reduction predicted from MIMS-measurements. The analysis was based on 23 data points from 3 different types of abatement technologies and resulted in a correlation coefficient (R^2) of 0.56. Although this is statistically significant ($P<0.001$), it is also clear that a more extensive dataset is needed for this purpose. Part of the difficulty with this approach is the inherent uncertainty associated with olfactometry.

Conclusions

Membrane Inlet Mass Spectrometry (MIMS) has been tested as a technique for continuous measurements of odour compounds in or emitted from pig facilities. MIMS is able to detect a range of compounds either as individual compounds or as groups of structurally related compounds. MIMS has been demonstrated to be sufficiently robust to be used on-site and to carry out measurements unattended for extended periods of time. Examples of MIMS-measurements include long-term monitoring of the efficiency of a biofilter installed in a pig facility and monitoring the effect of cooling ventilation air on the emission of odour compounds. A tentative comparison of MIMS with olfactometry indicates a potential for predicting odour reduction from MIMS-measurements, although more data is needed to confirm this.

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Understanding Biogenic GHG Emissions Using Long Path Fourier Transform Spectroscopy (LPFTS)

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Abstract

Biogenic GHG emissions resulting from biological processes at the microbial level can be considerably complex. Long Path Fourier Transform Spectroscopy (LPFTS) is a new evolving real time air pollution monitoring technique capable of detecting multiple pollutant gas signatures by measuring the transmittance [absorption] of light across a predetermined path.

Methodologies, protocols and algorithms developed at Trent University using LPFTS permit real time assessment of complex biogenic point source GHG as well as GHG precursor emissions.

Correlation of real time observational field data obtained to known biological processes allow us to achieve a better understanding of underlying microbiology and biochemistry as well as potential "natural" mitigation strategies such as anaerobic digestion of organic [biogenic] residuals.

Background

The industrialized signatories of the Kyoto Protocol have agreed to reduce their respective Greenhouse Gas (GHG) Emissions by an average of 5.2 % below 1990 emission levels. Protocol implementation has stimulated a new market where practices that reduce GHG emissions are "traded" for dollars with companies or countries that do not meet their target emission reductions. Key to equitable trading is independently verifiable determination of emissions mitigated. While industrial emissions from known processes are readily qualified as well as quantified, emissions due to biogenic processes are not always readily quantified due to the variable and complex nature of the processes themselves. Knowledge gaps exist in the areas of business as usual emissions that occur during decomposition of organic materials in uncontrolled environments such as field applied manures and controlled digestate emissions, where a complex mix of microbes are responsible for the decomposition of organic materials. If we "move" decomposition of organics into a fully controlled environment such as a digester, the substrate exits a fully enclosed vessel as stabilized digestate, emissions are voided and the organic energy potential can be harnessed in the form of biogas (65% methane and 35% CO_2).

The true potential to generate carbon credit trades by using anaerobic digesters for processing of surplus organic materials and surplus manures from agricultural sources have yet to be determined.

The digester or biogas reactor feeds on raw manure from livestock to generate biogas and fertilizer. The biogas is harnessed and used to generate both heat and electricity using cogen technology. The GHG emission savings are two fold from this process.

The first GHG saving is incurred by producing electricity from hydrocarbons that do not originate from fossil sources. Therefore every kilowatt-hour of electricity produced by using biogas as a generator fuel reduces our dependence on fossil sources and offsets a corresponding fraction of a kilowatt-hour of electricity that would otherwise have had to be generated by a process that results in 'additional' GHG emissions. The CO2 emitted as a result of burning biogas can be considered part of a closed loop, as the CO2 generated had been 'sequestered' previously during photosynthesis, and fed to livestock.

Additional GHG emission reductions are realized due to the controlled volatization and conversion of carbon during digestion. A portion of the carbon originally present in the manure is volatized and converted to CH4 and CO2 during the digestion process and potential of digestate to emit CO2 and CH4 is reduced accordingly. N2O emissions are also potentially reduced as shown in related studies (Chatigny et al, 2003 as cited in MPTWG, 2005). Since the global warming potential of CH4 and N2O are respectively 21 and 296 times that of CO2, a one-tonne reduction in N2O is equal to a 296-tonne reduction in CO2 (IPCC, 2001). Therefore there is great potential for direct mitigation of GHG's as well as generation of CO2 equivalent downstream emission credits. A significant research gap exists in the area of comparative analysis of emissions from land applied manure and digestate. Presented here is a detailed description of a measurement technique for qualitative understanding and then quantifying these reductions in the downstream emissions.

Methodology

Methodology for both qualitative as well as quantitative evaluation of GHGs and precursors has been developed to better understand emission and mitigation potentials.

Qualitative

In order to accurately understand the GHG and precursor GHG emissions it is important to observe all the emitted constituents without interfering with the natural conditions. Natural conditions include the influence of temperature, wind, rainfall, solar radiation etc. This is accomplished by using a Long Path Fourier Transform Spectroscopy (LPFTS) technique. A Fourier Transform Spectrometer (FTS) measures the amount of light at each frequency across a predetermined spectral interval. The common spectral interval utilized here is InfraRed (IR) radiation at 400 – 4000 wave numbers (cm^{-1}). Since molecules possess unique absorption features of IR radiation (or any radiation) the spectrometer is able to detect these constituents by monitoring the transmission of light across a predetermined path. The more molecules within the path, the more radiation absorbed within the molecules own unique region, as seen in Figure 2. The amount of absorption is mathematically represented by the following equation, which is known as the Beer-Lambert Law

$$I=I_o e^{\alpha v l C}$$

Where I = Intensity of light at a certain frequency after traversing path length l
I_o = The initial intensity of light at a certain frequency
α_v = The molar absorptivity of a constituent at a certain frequency
l = Path length
C = Concentration

In order to qualify differences in GHG emissions between raw and digested manure, the FTS is located between a field spread with raw manure and a field spread with digestate, as seen in Figure 1. Two mirrors are placed at the end of both fields. A broad band IR source sends light to the mirror where it is then reflected back into the spectrometer. The spectrometer measures the spectrum of light and the subsequent absorption features of every constituent present that absorbs light in this region.

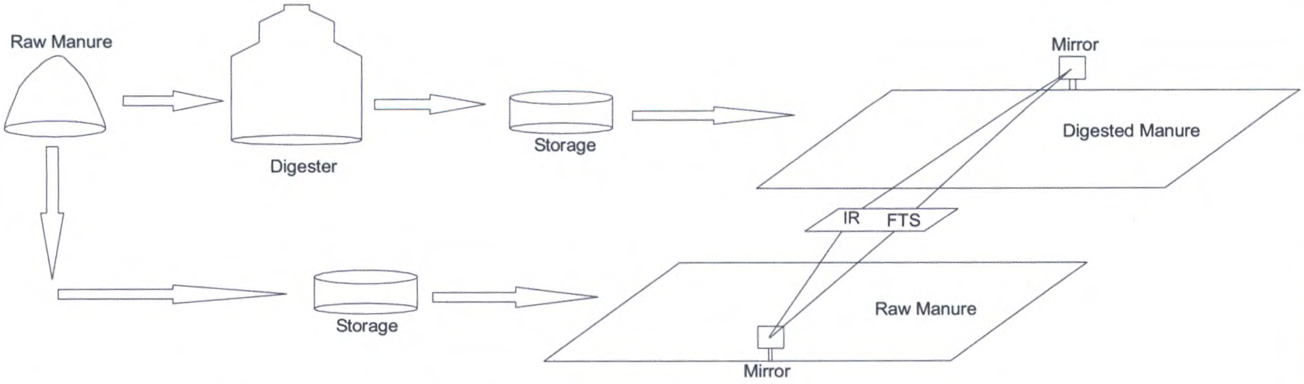

Figure 1: Shows an overview of the experimental configuration.

The path length is the distance to the mirror and back. Measurements are taken for both fields in real time. The measurements are then divided as in Figure 2 to demonstrate the percent difference in transmitted light and the corresponding difference in concentration. Meteorological conditions are measured throughout. Ideal conditions are when the wind direction is perpendicular to the path in which the light travels. This allows us to "see"(in terms of IR absorptions) the differences in concentrations for the two fields without disturbing the natural parameters outlined above. Path lengths are typically 200 m or more, in order to provide reproducible average concentrations and minimize variabilities associated with spreading manure. It is desireable that the two fields be level and that the two light paths be at the same distance and height above ground.

Quantitative

In order to quantify GHG and GHG precursor emissions and associated rates the same methodology is employed as in the qualitative configuration. Only this time micrometeorological parameters such as vertical and horizontal wind direction and speed are simultaneously logged at the same time. Furthermore additional paths at different heights and horizontal positions are monitored concurrently by other FTSs. This permits reliable visualization of air movements, resulting in concentration gradients for all recorded [emitted] GHGs and GHG precursors. This data can then be used to model emission rates for all IR visible constituents. A similar micrometeorological - gradient technique has been used to calculate emission rates in previous studies using point source sample collection at different heights. It has also been compared to a SF_6 tracer technique for reliability verification. The results and methodologies of this study are described in detail by Galle et al (2000).

LPFTS Simulated Results

Field measurements will commence in the spring of 2006 at the Lynn Cattle Farm, located just north of London, Ontario, Canada. Topography as well as soil characteristics are documented, well known, very homogenous and therefore close to ideal at this location. In order to bench test LPFTS performance prior to field measurements, simulations were carried out. The concentration values used within the simulations were based on a study conducted by Griffith et al (1999) where elevations in atmospheric CO_2, NH_3 and N_2O concentrations caused by land applied raw manure were simultaneously monitored using an FTS and a sample cell where the sample atmosphere was collected through Teflon tubing. The study showed that the elevation above the background concentrations for CO_2, NH_3 and N_2O were between 0-200, 0-0.4 and 0-0.125 ppmv respectively.

In order to obtain simulated result of what is expected using the measurement configuration outlined in the methodology section, simulations of transmission measurements over a raw manure spread field and digested manure spread field were created using the FASCD3 radiative transfer model (Clough et al, 1995). The concentration values used for digestate correspond to fully digested substrate i.e. background values, which are 1.8 ppmv, 365 ppmv, 50 ppbv and 310 ppbv for CH_4, CO_2, NH_3 and N_2O respectively. In order to simulate raw manure transmission measurement values of 50 ppbv, 200 ppbv and 25 ppbv and 10 ppbv above the background value were used for CH_4, CO_2, NH_3 and N_2O respectively. These differences in concentration values fall within the limits measured in the Griffith et al (1999) study. The value for CH_4 is assumed to be 50 ppbv. The two simulated measurements were then divided to give the percent difference in transmission of light at a spectral resolution of 0.125 cm^{-1} as shown in Figure 2. The path length used in the simulations was 200 m at a temperature of 20° C and a humidity of 40%. Figure 2 also shows a colour-coded display of the unique absorption features of CH_4, CO_2, NH_3, and N_2O. The concentrations of these constituents will be determined by matching the measured transmission difference to a simulated transmission difference. The concentrations required to make the simulation match the measured values will be equal to the concentration difference between the two fields. The plots in Figure 2 demonstrate that the above-mentioned constituents are easily detected and that lower concentration differences will also be seen. The limiting factor for lower detection limits is instrument-generated noise, which is illustrated in the error section.

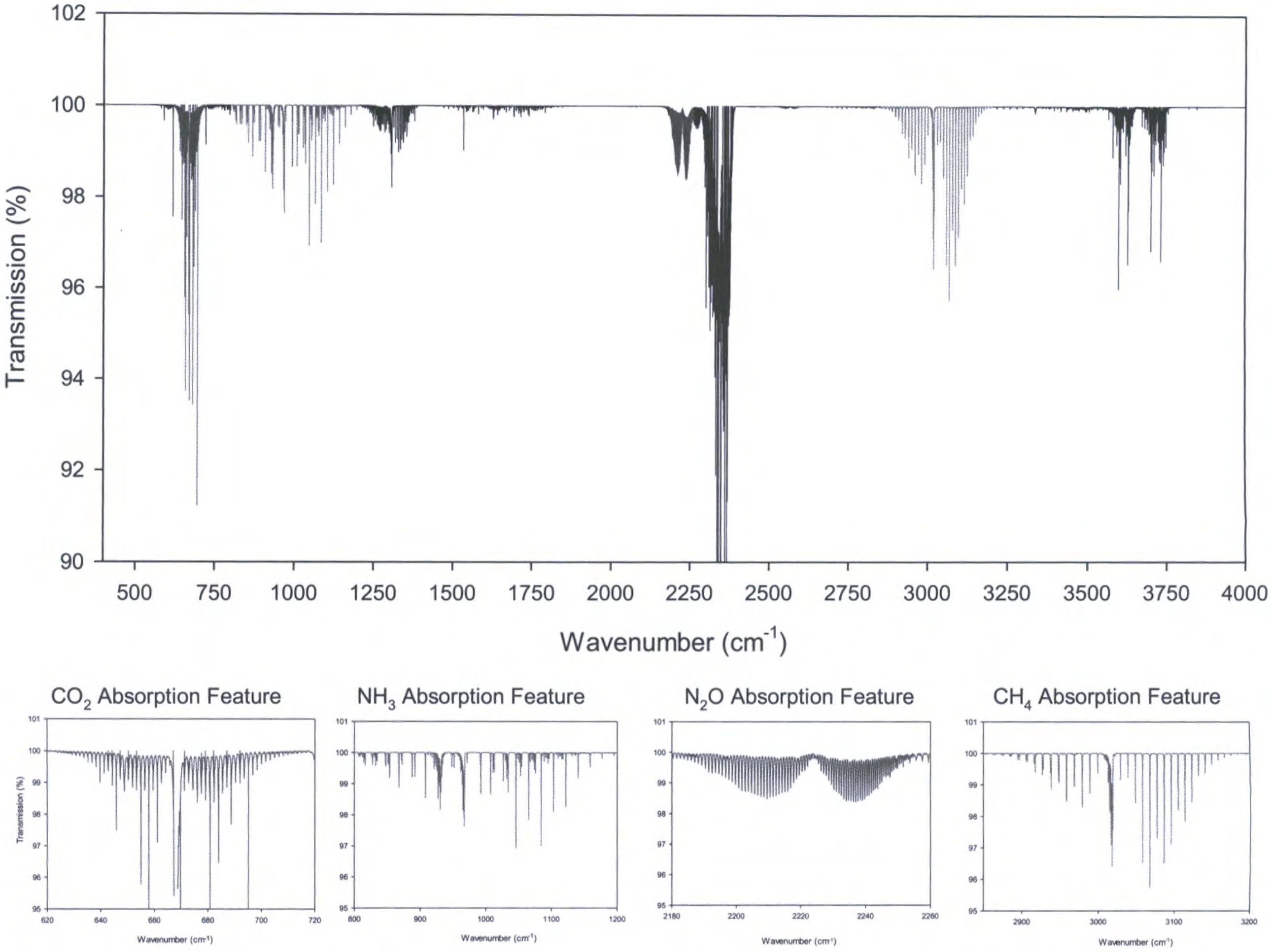

Figure 2: Shows the simulated difference in transmission of radiation between a raw manure spread field and a digested manure spread field. The bottom plots show each of the four constituents own unique absorptions.

Error Sources	Error (%)
Instrument Calibration	3.0
Instrument Noise	0.6 - 100
Cross sectional data	2.2
Total Error *	**3.8**

Table 1. Shows the contribution of the various error sources to the total error. Since each error source is independent of one another the total error is calculated by taking the square root of the sum of the squared error sources. * This total error is based on 0.6 % instrument noise and a 5-minute 0.125 cm^{-1} measurement.

LPFTS Error

The significant sources of error in LPFTS measurements can be: instrument calibration, instrument noise and in the cross sectional data used by the FASCD3 model. Table 1 quantifies the amount of error associated with each source.

The instrument noise contribution varies due to length of time and spectral resolution of measurement. The noise for two complete 5-minute measurements (digested and raw manure) equals 0.5921 % peak to peak at a resolution of 0.125 cm^{-1}. In the case where depth of the absorption feature is only 0.5% then the noise contributes 100 % error. Obviously the LPFTS method would not use such a peak. Figure 3 shows a typical absorption feature where noise would only contribute 2 %.

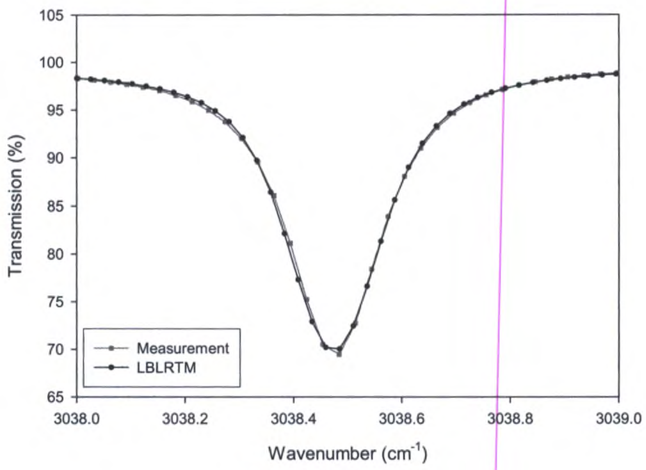

Figure 3. Shows the agreement between the measurement and the model for a single CH_4 absorption feature.

The noise value can also be improved by reprocessing the measurement at a lower resolution if the absorption feature in question does not require a high resolution to measure it accurately. Table 2 shows the various noise values for each part of the spectrum under different spectral resolutions.

Region (cm^{-1})	0.125 cm^{-1}	0.25 cm^{-1}	0.5 cm^{-1}
900-1100	1.055 %	0.665 %	0.295 %
2700-2900	0.592 %	0.373 %	0.165 %
4500-4700	0.563 %	0.355 %	0.158 %

Table 2: Noise values present in the combination of a 5-minute digestate measurement and a 5-minute raw manure measurement at three different spectral resolutions.

The error can be improved further by repeating the analysis procedure on multiple absorption features belonging to the atmospheric constituent in question. This will reduce the error by a factor of 1/sqrt(N) where N is the number of absorption features.

Discussion

From the simulated and measured instrument noise results it is evident that the LPFTS measurements technique will be able to detect the four constituents examined here at concentration differences as low as 10 ppbv. This accuracy is adequate when compared with previous measured results as seen in the Griffith et al study. Increased precision may be required during actual field measurements for digestate. This can be accomplished in several ways. The first is increasing the path length used in the measurement procedure. The LPFTS measurement technique is capable of path lengths up to 400 m. This is twice the path length examined here and would effectively doubles the absorption value for values close to zero. The second is increasing the number of absorption features used in the analysis. If a single absorption feature yields an error value of 3.8 % and 30 similar features are used to calculate the concentration of the constituent in question, the actual error value would be reduced to 0.7 %. Furthermore, instrument noise can be improved by reprocessing the measurements at a lower resolution as seen in the error section of this paper.

It should be noted that although only four constituents are examined here, the LPFTS measurement technique has the ability to simultaneously monitor all the emitted constituents that absorb radiation within the region being monitored.

Conclusion

In order to accurately quantify CO_2 equivalent credits generated by anaerobic digesters it is important to understand the downstream GHG reductions. Considering the global warming potential factors of some of the gases in question, generation of CO_2 equivalent credits in this area due to the process is potentially significant. The study to date demonstrates that the use of the LPFTS measurement technique has the potential to give a qualitative picture of the GHG and precursor concentration differences between land applied digestate and raw manure emissions without disturbing any natural parameters. This can then subsequently provide the data required to quantify the emission rate of each individual gas when coordinated with micrometeorological - gradient techniques.

With particular reference to manures, past emission models prioritized direct CO_2, CH_4, and N_2O emissions. The presented LPFTS methodology will enable definition and quantification of most if not all GHG precursors as well and assist in the development of an enhanced GHG emissions model with the potential to predict digester GHG mitigation performance based on correlation between microbial rates of digestion, carbon conversion and final emissions from digestate.

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Presence of Heavy Metals, Dioxin-like PCBs and Mercury in Fruit and Vegetables and Assessment of Air Quality in the Catania Territory

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Abstract

The European Community has given attention to monitoring heavy metals and PCBs because they cause different kind of pathologies. Through this study the Authors wanted to investigate some common products, largely consumed in the provincial territory, for heavy metals, dioxin and dioxin-like PCBs, taking into account also the different environment matrices (soil, water, air). Results have allowed a global evaluation on contamination of fruit and vegetables which has turned out to be generalised.

Introduction

Through the "11 October 2004 Recommendation" the European Community Commission has started monitoring the baseline levels of heavy metals, dioxin and dioxin-like PCBs. The attention of the European Community for heavy metals and PCBs is based on scientific evidence proving that they cause many pathologies at different levels. Moreover, for cadmium has not been excluded a cancerogenic effect, methylmercury and dioxin-like PCBs can be teratogen, nickel is cancerogenic.

Very important is also, to the Authors' opinion, the concept of "ALARA" (as low as reasonably achievable); though it is strictly connected to cultivation practices, it is also well applied to fruit and vegetables whose consumption nowadays is more and more advised to the population.

Based on this background the following research objectives were set:

- to verify the impact of using fertilizers on the presence of heavy metals in fruit and vegetables;
- to study possible correlations between use of compost and presence of dioxin-like PCBs, taking into account also the different environment matrices (soil, water, air);
- to assess the presence in the aforesaid matrices of Vanadium and Selenium that seem to protect people from diabetes, renal stones and cardiac arrhythmias; to analyse air samples in order to confirm the eventual reduction of lead in the same matrices.

Methods

In each area, samples have been taken from:

- fruit and vegetables of wider consumption in the provincial territory (solanaceous, cereals, leaf vegetables, grape);
- soil, water and air. After samples mineralization, metals quantitative determination was carried out in atomic absorption spectroscopy. After purification and extraction (EPA) determination of PCBs and of dioxin-like PCBs has been carried out by means of GC technique in ECD.

Air samples have also been analyzed through SEM with EDX.

Results and Discussion

No mercury nor PCBs were found in examined samples. Other metals were most of the times present though in moderate amount.

Results have allowed a global evaluation of metal contamination that, even though within legal limits, turns out to be generalized. A remarkable contribution comes from the atmospheric contamination that has been carefully weighted.

Conclusions

The integrated approach, that is the basic principle of the "White book" on alimentary safety, is the only winning strategy to assure more and more alimentary safety and consumers' protection; it promotes education and involvement of all alimentary chain stakeholders.

Budget Estimates of Indoor Air Pollutants from Solid Biomass Fuels Used in India

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Abstract

In developing countries the most important indoor air pollutant are the combustion products of solid biomass fuels such as fuel wood, dung cakes, crop residues and charcoal. Almost 50% of the world's population and upto 90% of rural households in developing country rely on biomass fuels. It has been estimated that about half a million women and children die each year from indoor air pollution in India. The combustion of biomass release complex mixture of various species viz., NOx, SO_2, organic carbon (OC), elemental carbon (EC), Polycyclic Aromatic Hydrocarbons (PAH), Non-methane Hydrocarbons (NMHC) and Volatile Organic Compounds(VOC). Efforts have been made to study the emissions from solid biomass fuels to evaluate their emissions factors and derive budget estimates for India. An experimental setup has been built to carry out controlled burning of biomass fuels similar to the residential application (small cooking stoves and an open burning) in India. The emission factors for NOx, SO_2, OC, EC, PAH, NMHC and VOC have been evaluated. The preliminary budget estimates from biomass fuels in India for above species are 0.3, 0.8, 2.0, 0.7, 0.01, 2.8 and 1.4 Tg, respectively.

Introduction

Fuels used in residential sector of India is a major component of total energy use in India. Type of fuels used in residential sector in India varies with different environment and availability of the local fuels and also by way of cooking food in the open fires or in the rural cook stoves (Earthen Chulas). Out of residential fuels, 70 to 80% of the energy needs in rural India are met with the use of biomass in the form of fuel wood, dung cakes, charcoal and agricultural residue. Burning of biomass from all these sources is well known to be associated with the emission of smoke/plumes consisting of particulate and gaseous species as these are not energy efficient processes and thus the fuels are not burnt completely. The species emitted and their concentrations depend on the nature of the source of biomass and other factors including the physical parameters associated with the consumption of the biomass.

Poor kitchen ventilation i.e., lack of properly designed and installed chimneys or exhaust, is common in rural areas in India. This together with the low efficiency cookstoves and large amount of fuels used results, in many cases, in serious indoor air pollution. High concentration of CO, NO2, PM and benzopyrene were found indoors with the highest values at standing breathing level in the kitchen when dungcake, fuelwood and coal were burning (Kandpal et al., 1995a and 1995b). Personal exposure to the toxic air pollutants thus may greatly increase due to the high emission from domestic use. WHO asserts a "Rule of 1000", which states that a pollutant released indoors is one thousand times more likely to reach people's lung than a pollutant released outdoors (WHO, 1997). In recognition of the need to identify and develop cleaner domestic combustion systems, this study aims at providing an initial assessment of total emissions from indoor combustion in the rural sector of India.

Comprehensive studies to evaluate the emission factors for OC, EC, SO_2 and NO_x for biofuels used as energy source in rural residential sector have been carried out to arrive at reliable budgets estimates. PAH, NMHC and VOC's are of special interest due to their toxicity, carcinogenicity and ubiquitous presence in the environment. Thus the studies are being carried out on some important PAH, NMHC's and VOC,s and would be presented at the workshop.

Experimental

The experimental setup consisting of a U-shaped chimney (see Firgure-1) to carry out biofuel burning in the laboratory with all the plumes passing through the High Volume Sampler (HVS). A Whatmann 8×10 sq. inch GF/A filter is fixed on the support for the collection of particulate matter. The other end of the chimney is about 25 cm above the ground. Known quantity of fuel is burnt below the chimney and the plumes pass through the HVS. The chimney is fixed tight on to the HVS to ensure complete deposition of the particulate matter emitted during the burning of the fuel sample. Part of the plumes are routed through the impingers in series for the sampling of SO_2 and NO_X. They are evaluated by wet chemical methods. The particulate matter deposited on the filter paper is analysed for EC and OC. For the determination of PAH, VOC and NMHC from the emissions studies are being conducted. A known amount of fuel is kept on a firebrick support with an electric filament mounted on it to initiate the burning of the fuel. Fuels emit smoke as a result of pyrolysis in the initial stage. When the temperature rises enough it burns with vigorous flames for some time and ends up in smoldering for a few minutes. The three stages i.e., pyrolysis, flaming and smoldering, together are referred to as combustion. The fuels studied are fuel wood, dung cakes, agricultural residue and charcoal. This burning setup is very similar to the style of cooking or residential heating adopted in rural sector or small-scale industries except for the difference that instead of the electric heater plate some stand is used, which keeps the fuel a little risen above the ground. Sometimes in residential cooking the fuel is burnt on the ground between two bricks or in a three sided fire place i.e., a typical Chulha (an earthen stove used for cooking in villages) or in cylindrical fire place with raised hearth made of a steel mesh and having provision for air inlet beneath it. The details of the experimental setup are described in the earlier papers (Gadi et al., 2003, Parashar et al., 2005).

Results and Discussion

Emission factors of SO_2, NO_X , OC and EC as determined in the laboratory have been given in table 1. The emission factors are based on experiments which resemble a typical burning/cooking process. There is a degree of natural variability in fuel quality depending upon region and seasons, which has led to a range for each emission factor. It is seen that emissions of SO_2 are highest from dungcakes and low from agricultural residue and charcoal, but NO_X emissions from bagasse are almost double those from fuelwood and charcoal. The emission factors for OC and EC are highest for dungcakes and lowest for charcoal. Emission factors for bagasse have been used for evaluation of emissions from agricultural residues. The emissions depend upon the combustion characteristics and would be smaller with the increase in burning efficiency. The annual consumption of Fuelwood, dungcakes, agricultural residue and charcoal are 281 Tg, 62 Tg, 36 Tg and 3 Tg respectively (Venkataraman et al., 2005 and TEDDY, 2001/2002).

Table 1. Emission factors for SO_2, NO_X, OC and BC from biomass fuels used in India

Bio-Fuels	SO_2 (g/kg)	NO_X (g/kg)	OC (g/kg)	BC (g/kg)
Fuelwood	0.7± 0.6	2.2± 1.0	3.5± 1.9	1.1± 0.5
Dung cakes	1.4± 0.9	0.8± 0.6	12.6± 4.5	4.4± 2.2
Agri. Residue	0.5± 0.5	3.3± 0.9	3.9± 3.4	1.3± 1.1
Charcoal				
Production	-	0.1± 0.1	18	1.4
Consumption	0.5± 0.3	2.1± 0.5	0.9± 0.6	0.4± 0.2

Using the emission factors given in Table 1 and the annual consumption of various biomass fuels in India, the budgets of SO_2, NO_X , EC and OC are estimated (Table 2). The major contributors of the emissions are fuelwood and dungcakes due to their high annual consumption in the rural residential sector.

The experimental work on the estimation of PAH, NMHC and VOC is being carried out. The preliminary budget estimates based on the emission factors from literature (Oanh et al., 1999 and Andreae and Merlet, 2001) for PAH, NMHC and VOC are 0.01, 2.8 and 1.4 Tg respectively. Further work is in progress to improve the reliability of all the emission estimates by conducting experiments on different biomass fuels being used as a fuel in the residential sector for cooking purposes in different regions of India.

Table 2. Budget estimates for SO_2, NO_X, OC and BC from biomass fuels used in India

Bio-Fuels	SO_2 (Gg)	NO_X (Gg)	OC (Gg)	BC (Gg)
Fuelwood	197±169	618±281	984±534	332±151
Dung cakes	87±56	50±37	781±279	273±136
Agri. Residue	18±18	119±32	140±122	47±40
Charcoal				
Production	-	0.3±0.3	54	4.2
Consumption	1.5±0.9	6.3±1.5	2.7±1.8	2.4±1.2
Total	304±244	794±352	1962±937	659±328

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Environmental and Management Drivers of Nitrous Oxide Emissions in Australian Agro-ecosystems

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Abstract

Australian climate, soils and agricultural management practices are significantly different from those of the northern hemisphere nations. Consequently, experimental data on greenhouse gas production from European and North American agricultural soils and its interpretation are unlikely to be directly applicable to Australian systems. A program of studies at five sites of nitrous oxide greenhouse gas emissions from agriculture has been established by the Co-operative Research Centre for Greenhouse Accounting. The study is designed to reduce uncertainty of non-CO_2 greenhouse gas emissions in the Australian National Greenhouse Gas Inventory and provide outputs that will enable better on-farm management practices for reducing nitrous oxide greenhouse gas emissions. As part of this study are experiments with both chamber and micrometeorological emission measurement techniques which focus on process based studies of emissions and paddock scale emissions respectively. As well there are parallel studies on emission modelling and good practice. The systems being examined and their locations are irrigated pasture (Kyabram Victoria), irrigated cotton (Narrabri, NSW), irrigated maize (Griffith, NSW), rain-fed wheat (Rutherglen, Victoria) and rain-fed wheat (Cunderdin, WA). The field studies include treatments with and without fertilizer addition, stubble burning versus stubble retention, conventional cultivation vs. direct drilling and crop rotation to determine emission factors and treatment possibilities for best management options. The data to date indicate that nitrous oxide emission factors (the nitrogen lost as nitrous oxide as a fraction of the fixed nitrogen applied) for inorganic nitrogen fertiliser and urine from animals are profoundly affected by the climatic variations in soil water status and soil temperature. The emission factors are much lower than previously used for rain-fed wheat and significantly higher for irrigated maize with stubble burning. Application of nitrogen fertilizer at different rates to irrigated cotton indicates the non-linear growth in nitrous oxide emissions when nitrogen application exceeds plant uptake requirements. These new emission factors are applied to produce the spatial distribution of nitrous oxide emissions in Australia. There are substantial changes to the distribution of emissions compared to the spatial distribution of nitrous oxide emissions obtained using the IPCC default emission factors. The good practice management options that have been identified so far include stubble retention (in maize), crop rotation in cotton, and matching the nitrogen applied to the crop nitrogen requirements.

Efficacy of a Lagrangian and a Gaussian Model for Back Calculating Emission Rates from Feedyard Area Sources

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Abstract

Emissions of odor, gases and particulates from animal and crop production systems are an expected by-product of the systems. With the decrease in traditional setbacks, increasing community expectations and increasingly stringent federal and state air pollution regulations, agricultural operations have had to rethink traditional operating procedures.

As a part of this "rethink," baseline data on emission rates is needed to establish generic or even site-specific emission rates. The way in which emission rates (ERs) from lagoons and feed pads are determined is subject to debate. The two most commonly used styles are referred to as direct and indirect techniques. Direct methods involve placing enclosures on the surfaces to measure the emissions. Indirect methods refer to taking downwind samples on or near a source and calculating an emission rate using mathematical formulae. Indirect techniques offer the advantage of being able to process relatively large sources, such as lagoons and feedyard pens, and provide a spatially integrated emission rate. A possible disadvantage to using back calculation techniques is that there may be variation between the emissions derived using different types of indirect techniques.

Hydrogen sulfide emission rates were determined at two feedyards using two indirect back techniques, the Lagrangian WindTrax model and the Australian Gaussian plume model, Ausplume, which is based on the USEPA ISC model. Both models were run using the same data set and default dispersion settings. This was undertaken as to provide a comparison of the models as used with default values. Between 24 and 33 points were modeled at each site, providing an average emission rate over time. Each data point consisted of upwind and downwind concentrations, wind speed, wind direction and atmospheric stability data.

At present it is unknown which of the models provides a "true" estimate of emissions from area source. However, the models compared very well for the data sets. For feedyard A the relationship between the models was $y = 0.9x - 0.1$, $r^2 = 0.98$ for the pond, and $y = 0.9x - 1$, $r^2 = 0.99$ for the pens. A similar relationship was observed for feedyard C with $y = 1.2x - 0.8$, $r^2 = 0.99$ being observed for the pond data. As shown by the similarity of the gradients, the average emission rate and standard deviation of the predicted concentrations was similar.

Differences in the modeled predictions were identified as a function of distance from the source to the measurement point and subtle differences in the models. The results show that the WindTrax and Ausplume (ISC) models provided very similar emission rates for three real world data sets. This indicates that emission rates derived using one model can be used within other models with a reasonable degree of confidence.

Introduction

Emissions of odor, gases and particulates from animal and crop production systems are an expected by-product of the systems. With the decrease in traditional setbacks due to urban encroachment, increasing community expectations and increasingly stringent federal and state air pollution regulations, agricultural operations have had to rethink traditional operating procedures and even traditional areas of operation.

Area sources, including feedyards, are amongst the most difficult sources from which to estimate gaseous emission rates (Watts 2000). This is due to the fact that there is no way of directly measuring or sampling the emission. Therefore, indirect methods must be used where the emissions are sampled after they have mixed with the air stream (Watts 2000). Currently a number of methods are available to determine emissions from area sources; however, it is important to note that in these techniques there are a number of inherent uncertainties.

At present, there are two broad areas used to determine emission rates from area source. These are indirect, also known as back calculation, or direct, such as wind tunnels and flux chambers. Many studies have been undertaken using flux chambers, wind tunnels and back calculation techniques, however it is hard to define which of the techniques actually provides a realistic emission rate.

If the end use of the data is dispersion modeling (i.e. predicting concentrations away from a source using computer models) it is essential that the direct techniques would provide the same emission rate, i.e. those derived using a model using downwind concentrations would be the same as a direct technique used at the same time. The advantage offered by back calculation is that it can provide a spatially averaged emission rate (Harris *et al.*, 1996; Smith and Kelly, 1996) rather than a single point sample of a source based upon the limited footprint of an enclosure technique. A number of assumptions must be made when using Gaussian or other models to estimate emissions. Some of the assumptions detailed by Harris *et al.* (1996), which are relevant for this work include:

- the ground is a barrier to vertical mixing and is represented as a flat surface reflecting the plume back into turbulent air flow;
- the emission is neutrally buoyant – this assumption implies that the temperature at which the gas is released equals the ambient air temperature;
- the gas does not degrade after release (conservation of mass);
- gas source emissions do not vary within the averaging time used in the model; and
- gas source emissions do not vary spatially.

In this study, two models, the Australian Gaussian model Ausplume (Lorimer, 1986) and the Lagrangian model WindTrax (Flesch *et al.* 2005a, 2005b) were run on identical real world data sets to derive hydrogen sulfide emission rates at two large feedlots in Texas.

Methods

Sample Sites

Both beef cattle feedyards were located in the Texas Panhandle, in a semi-arid region with average annual rainfall of 500 mm. The feedyards were open-lots with earthen-surfaced pens. Pen slopes ranged from 1 to 5%.

Feedyard A had a one-time capacity of 18,000 head, while Feedyard C had a capacity of 55,000 head. Both had average stocking densities of one animal per 14 m^2 (150 ft^2). Animal weights ranged from 180 to 550 kg, with an average of about 340 kg. Cattle in both feedyards were fed a 90-92% concentrate diet consisting primarily of steam-flaked corn with 7-10% roughage consisting of ground alfalfa. The diets contained Rumensin® and Tylan®. About 15% of the steam-flaked corn was replaced with corn gluten feed in Feedyard C.

Meteorological Data Collection and Analysis

A 2 meter stationary meteorological station (Unidata America, Lake Oswego, OR) was located at each site, and recorded wind speed, wind direction, net solar radiation, and air temperature at a time step of two minutes. The stations were located on the edge of each feedlot approximately 100 meters (300 feet) from the feedlot pens in a field surrounded with low grass. Wind direction was scalar averaged for a 6 minute time period (2 minutes before and 2 minutes after) to obtain a representative wind speed and direction for modeling. Solar radiation and temperature were averaged over a 10 minute period to provide a representative radiation measurement.

Atmospheric Stability

Atmospheric stability was calculated using the solar radiation/delta-T (SRDT) method as detailed in USEPA (2000). The method uses the basics of Turner's (1964) method while negating the need for observations of cloud cover and ceiling. The method uses the wind speed (measured at or near 10 m) in combination with measurements of total solar radiation during the day and a low-level vertical temperature difference (DT) at night (USEPA 2000).

As 10 meter wind speed and direction data was unavailable, , the SRDT method was modified so that the wind speeds detailed in Table 6-7 in Meteorological Monitoring Guidance for Regulatory Modeling Applications (USEPA 2000) were useable with 2 meter data . To achieve this, the power law (Equation 1) was used to adjust the wind speeds from 10 to 2 meters based on the stability class in the table. The values for atmospheric stability class based on the new values for wind speed are shown in Table 1.

$$U_Z = U_{ref}\left(\frac{Z}{Z_{ref}}\right) \qquad \text{Equation 1}$$

where U_z is the wind speed at a height of Z (m) above the ground; U_{ref} is the wind speed at anemometer height Z_{ref}; a is the wind profile exponent, and is a function of the stability class.

Table 1: Adjusted wind speeds for SRDT determination

	Solar radiation (W/m^2)						
Wind speed at 2 meters (m/s)	≥925		925-675		675-175)		<175
<1.8	A	<1.8	A	<1.8	B	<1.6	B
1.8-2.7	A	1.8-2.7	B	1.7-2.6	C	1.6-2.4	D
2.7-4.5	B	2.7-4.5	B	2.6-4.3	C	2.4-3.9	D
4.3-5.1	C	4.3-5.1	C	3.9-4.7	D	3.9-4.7	D
≥5.1	C	≥4.7	D	>=4.7	D	≥4.7	D

The Ausplume Model

Ausplume is the accepted regulatory Gaussian plume dispersion in Australia and New Zealand and is based on the ISC model of Bowers *et al.* (1979). It is designed to predict ground level concentrations or deposition of pollutants emitted from one or more sources including area sources, volume sources or stacks.

Recently the model was upgraded to incorporate a numerical integration approach for area sources. This allows standard and irregular shapes (such as polygons) to be modeled with more accuracy close to the source. This option was used for the modeling. An example of the output from the model is shown in Figure 1.

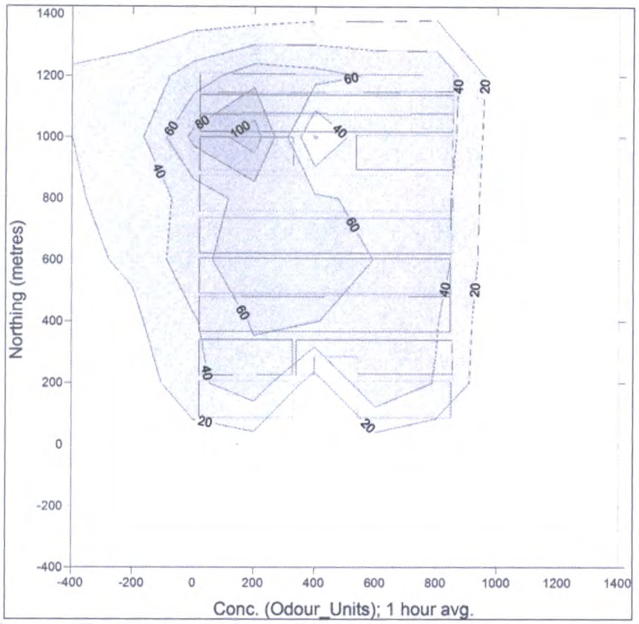


Figure 1. Example of pen alignment in Ausplume

Modeling was undertaken using an arbitrary constant emission rate of 1 ug/m^2.sec and using the default Pasquill Gifford dispersion curves for averaging periods of 1 hour. As an arbitrary emission rate was used, the emission rate had to be scaled to match the measured concentration thus providing an accurate estimate of the real emission rate. This was achieved using Equation 2.

$$ER = \frac{ER_{const}}{C_{\mathrm{mod}}} \times C_{meas} \qquad \text{Equation 2}$$

Where ER is the emission rate µg/m^2.sec, ER_{const} = the arbitrary emission rate (1 µg/m^2.sec), C_{mod} is the average modeled concentration at the receptor during the sampling period (µg/m^3) and C_{meas} = measured concentration at the receptor. The measured concentration was calculated as the downwind H_2S concentration minus the upwind H_2S concentration in µg/m^3.

The WindTrax Model

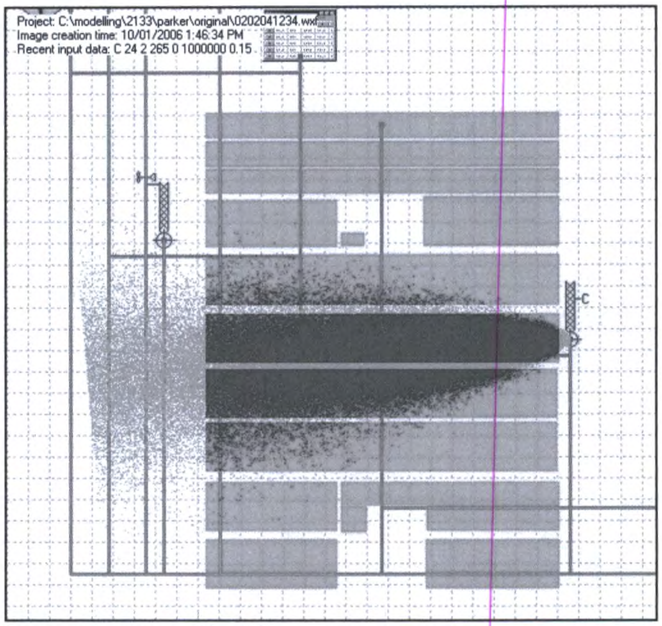
WindTrax version 2 (see Flesch *et al.* (2005) or Flesch and Wilson (2005) for details) was used to determine average emission rates.

WindTrax is a backward-time Lagrangian stochastic (BLS) dispersion model that calculates emission rates of gas from a source area based on measured wind speed and gas concentrations. WindTrax uses a Lagrangian (particle-following) model to simulate atmospheric dispersion. The model releases a large number of computational particles from a set location and follows their trajectories as they float passively through the surrounding air. To imitate the turbulent nature of the atmospheric surface layer, random forcing terms in the equations governing their motion disturb the particles. Although the path taken by each particle is therefore random, the average motion of the entire group closely matches that of the real atmosphere.

When a particle's trajectory causes it to bounce off the surface within an area source, it is assumed to represent the tracer emitted from the source. The more times a particle touches down within the source area, the greater will be its contribution to concentration measured downwind. WindTrax keeps track of these touchdowns and uses them to calculate the relationship between emission rate and concentration: if either is known, the other can be predicted.

When modeling emissions from area sources, it is generally much more efficient to follow particles backward through time from the measurement location back to the area source rather than predicting where a particle will go as it flows after being emitted from a source. This is because an area source represents a much larger target than does a point sensor; a given particle is much less likely to reach any specific detection point located downwind of its source than to have originated somewhere within an upwind area source, given that it ended up at the detector.

Prior to running version 2, version 1 of WindTrax was run. Both versions provided identical emission rate estimates. The location and size of the pens were defined with data taken from a scaled aerial photograph of the site. The inputs required by the model are similar to those described for Ausplume above. WindTrax was run using 1,000,000 particles to ensure good coverage of the source. The model provides the user with an emission rate in μg/m^2.unit time. An example of the pen shown in Figure 1 as set up in WindTrax is shown in Figure 2.



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Project: C:\modelling\2133\parker\original\0202041234.wxf
Image creation time: 10/01/2006 1:46:34 PM
Recent input data: C 24 2 265 0 1000000 0.15
```

Figure 2. Example of pen alignment in WindTrax

Surface Roughness

Roughness height allows the modeler to represent the presence of features in the surrounding area. Generally, the higher the surface roughness the higher the back calculated emission rate. Therefore, variation in this parameter makes it important for dispersion modeling. Kelly *et al.* (1994) investigated the aerodynamic roughness of an Australian feedlot in the 1990s by examining surface roughness using vertical temperature and wind speed profiles.

When applying the 1/10th rule of thumb, they expected a 15 to 20 cm surface roughness: in reality they found that the cattle and fences did not overly influence the surface roughness of the feedlot. Their work found the surface roughness to be 1.16 ± 0.3 cm. Based on their findings, the modeling was undertaken using a surface roughness of 5 cm in an attempt to compromise between the work of Kelly *et al.* and the 1/10th rule of thumb. Therefore, the results of the model predictions should fall within the range of this maximum and minimum expected surface roughness. As the primary focus of this work was to compare the models, the influence of surface roughness would remain the same provided both models used the same surface roughness values.

Data Used for Modeling

Dispersion models in general have a basic set of data required to run them. As a general rule the more complex the model, the more data required. In this case the data required was:

- Wind speed;
- Wind direction;

- Pasquill Gifford stability class;
- Surface roughness;
- Feedyard dimensions including pen dimensions;
- Sampling location and height; and
- Upwind and downwind concentrations in μg/m^3 (upwind concentration was subtracted from the downwind concentration).

Both models were run using the same data set and conditions with the exception that in Ausplume the pens were set as to have a 10 cm height above the surrounding area and an initial mixing height of 0.5m both of which are was not required to model using WindTrax.

Results and Discussion

The model was run on two feedlots for pen emissions and for a sedimentation pond at one of the feedlots. The results of the model comparison for the pen and pond data are shown for Feedyard A in Figure 3 and Feedyard C pond in Figure 4. Additionally, the combined data for both Feedyards A and C are presented in Figure 5.

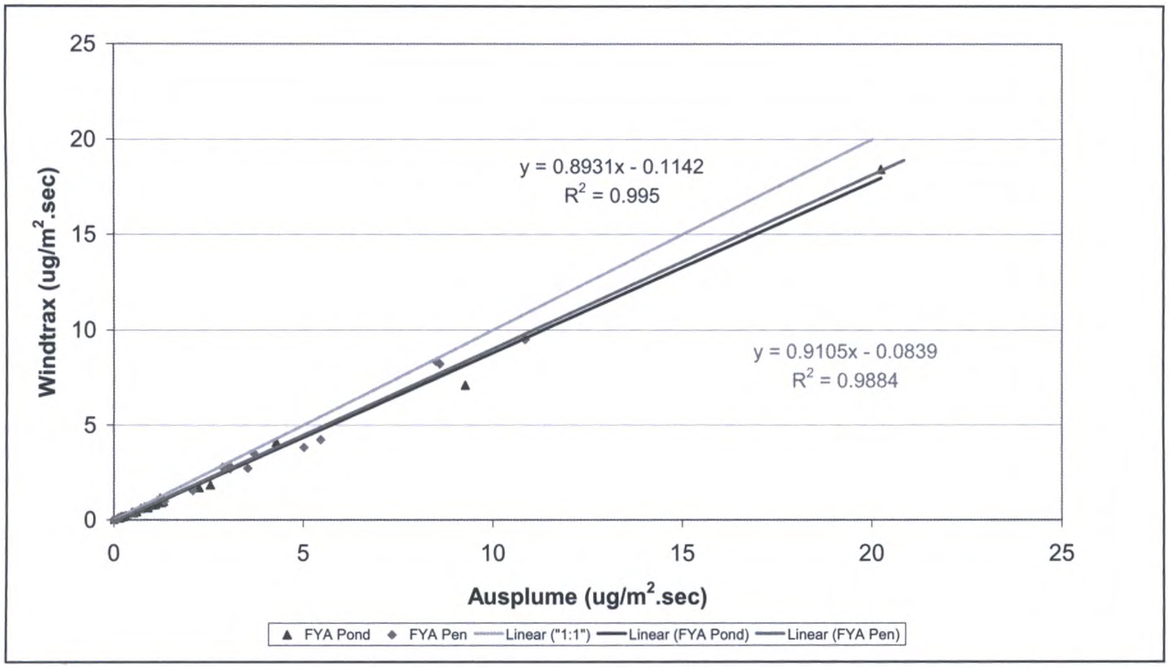

Figure 3. WindTrax and Ausplume derived emission rates: Feedyard A

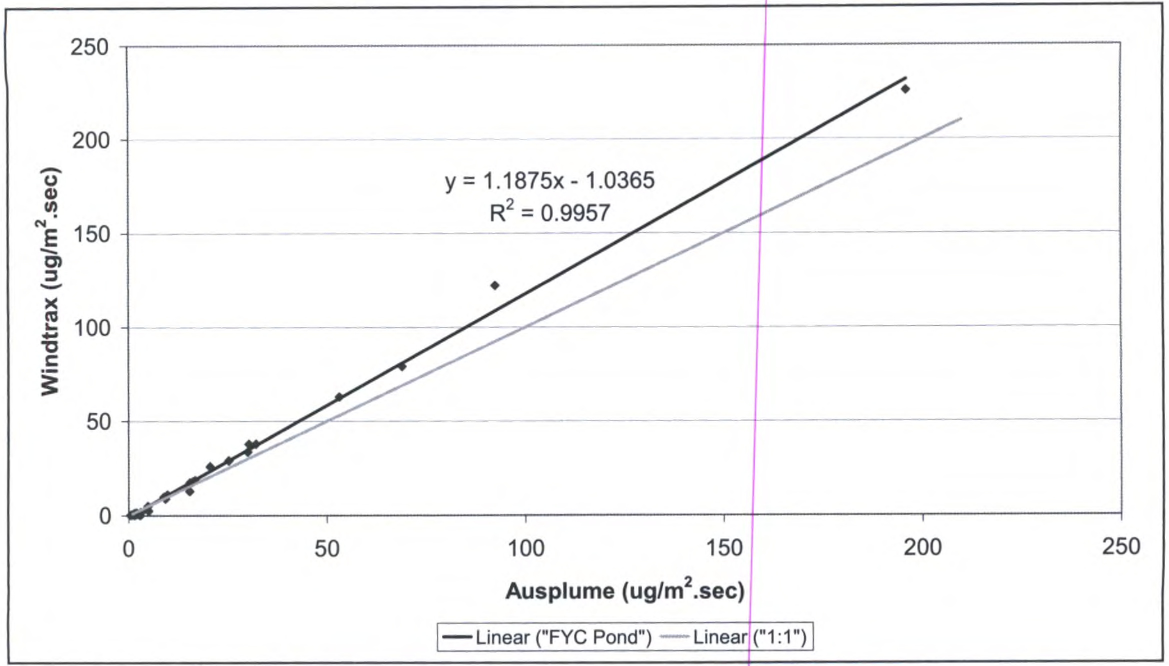

Figure 4. WindTrax and Ausplume derived emission rates: Feedyard C Pond

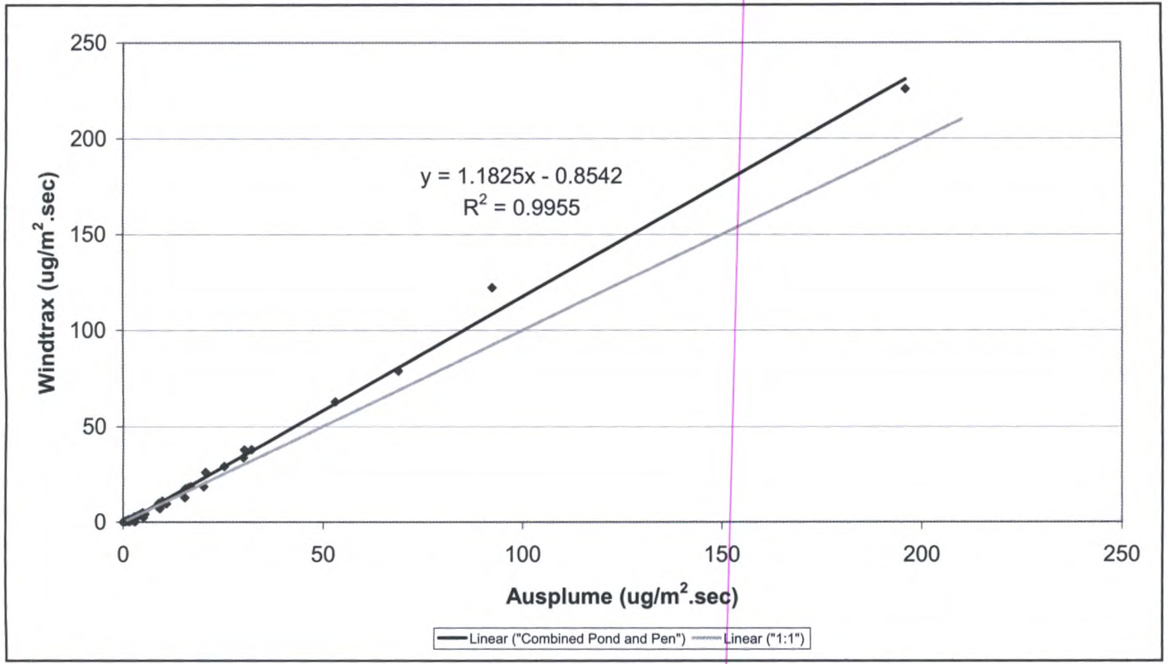

Figure 5. Combined data

It should be remembered that the Ausplume model, like all plume models is based on the Gaussian approximation, which assumes that a plume will disperse according to the normal distribution. In contrast to this the WindTrax model is a largangian model that follows randomly traveling particles in the air to simulate atmospheric dispersion. Thus, it is expected that there will be some differences between the models. Taking this into account, and inputting the same data into them, it would be expected that they would provide a similar if not identical response (i.e. 1:1, WindTrax : Ausplume). A good correlation was observed between the emission rates derived using the two models for both pond and pen data. This is similar to the work of Sommer *et al.* (2004) who found that the Theoretical Profile Shape (TSP) model and WindTrax correlated well.

The emission rates derived for Feedyard A via modeling (Figure 3) showed that the models predicted similar emission rates for both the pen and pond data sets (i.e. both had similar equations and r^2 values). However, Ausplume predicted slightly higher emission rates compared to WindTrax. Additionally, when all pond and pen data for both feedyards was combined (Figure 5), the data again showed a good correlation between the Ausplume and WindTrax derived emission rates. However in this instance, WindTrax predicted higher emission rates compared to Ausplume. When all of the data was combined the data was dominated by the higher emission rates derived for the Feedyard C pond which in turn had an influence in the derivation of the overall equation as shown in Figure 5.

Whilst a good correlation was expected the amount of deviation from the theoretical 1:1 line was not expected to be in the order of 20 %. This was unexpected as the two methods are essentially the same in that both derive an emission rate using a mathematical formula, which is linked to the input data. Previous studies have undertaken sensitivity analysis with regards to the effect of varying the model inputs. Important inputs for both models include wind speed, stability class, wind direction and surface roughness.

For each model run, both models used the same data, thus differences in with regard to difference the input data can be ruled out. The way in which the models process the data is therefore an obvious area for further investigation as the two models are different and thus will treat the data differently.

As shown in Figure 3 above, both models compared well irrespective of source size (pens maximum upwind fetch was approximately 3000 ft, ponds up to 2400 ft), thus source size may not have a direct influence in this instance. Possible reasons for the discrepancies between the models are discussed further below.

Stability class is an important input in modeling. An analysis of all of the data points showed that of the modeled data points, stability class A occurred 1 % of the time, class B 23 %, class C 28 % and Class D 49 % of the time. Thus neutral conditions occurred at approximately half of the sampling events. The data when correlated according to stability class is shown in Figure 6.

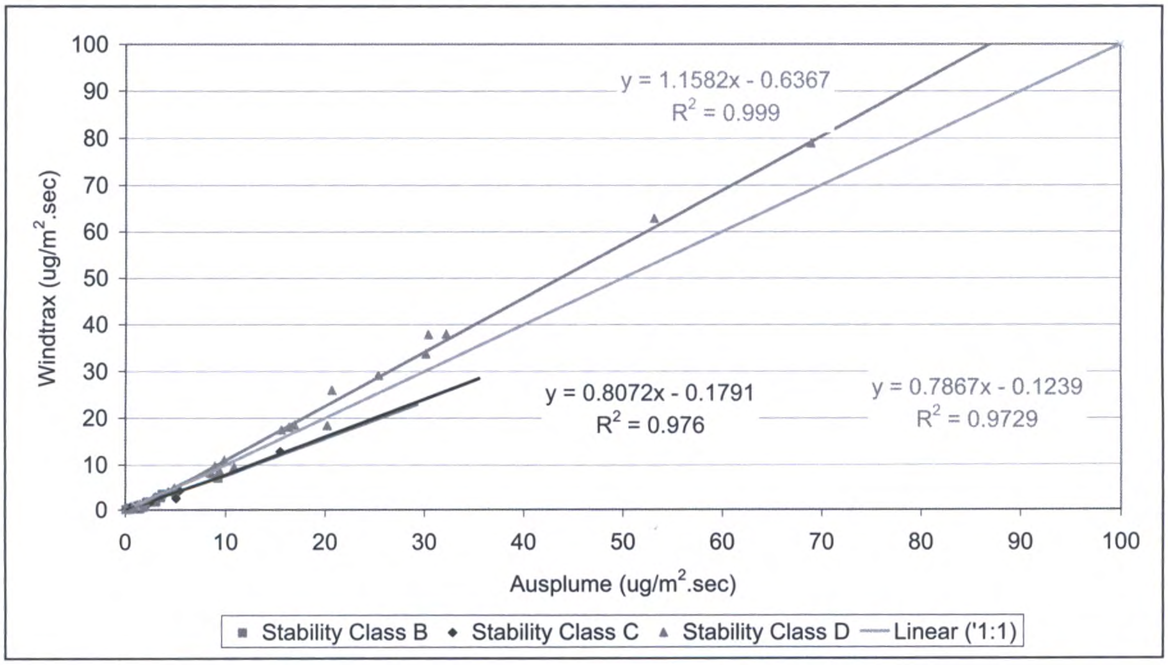

Figure 6. Emission rates as a function of Atmospheric Stability

Figure 6 shows that good correlations were observed between the models for the different stability class conditions. Interestingly, the results for stability class B and C events (unstable conditions) were very similar, however those for neutral conditions (Class D) resulted in higher emission rates (some emission rates were greater than 20 μg/m^2.sec) which may simply be a function of the amount of gas emitted from the source. Thus, from the data it can be concluded that under unstable conditions Ausplume tends to over predict emissions, whereas under neutral conditions Ausplume appears to under predict emissions compared to WindTrax.

Trinity Consultants (2000) concluded that ISC (upon which Ausplume is based) does not model unstable atmospheric conditions accurately. Whilst the emission rate data derived under neutral conditions was much higher than those under unstable conditions, the correlation between WindTrax and Ausplume was very good indicating that the models (including ISC) would provide similar estimates under neutral conditions. Further examination of the data in Figure 4 where WindTrax over predicted emissions compared to Ausplume showed that the emission rates derived were not a function of neutral conditions as only 32% of the dataset consisted of stability class D events meaning that a factor other than stability class is likely to have resulted in the difference in the predictions of the two models.

The modeling was undertaken as using a scaling factor (Equation 2) to enable back calculated emission rates to be derived using Ausplume. It is important to note that the meteorological data covered a period of approximately 6 minutes. This is handled well in WindTrax as in effect, it assumes that the data is all collected over the same averaging period. Additionally WindTrax uses the Monin-Obukhov Similarity Theory (MOST) for the Profiles in the atmospheric surface layer which is suitable for short time periods (Flesch *et al.* 2005 b). Ausplume uses the Pasquill Gifford dispersion curves that were developed from 10 minute averaged experimental data and are more commonly used for hourly averaged data.

It is likely that the comparison between the models could be improved by incorporating sigma theta (standard deviation of wind direction) data in Ausplume where an averaging time that is approximately the same as the time over which the data was measured (Environmental Protection Agency, 2000). However, the aim of the exercise was to compare the models using default dispersion settings thus future work should examine the improvement in emission estimation as a function of more representative dispersion curves in both models.

An easily identifiable difference between the Feedyard data sets is the distance from the source to the measurement locations. For Feedyard A (pens and ponds), most of the measurement sites were located within 50 feet of the source (pens and pond), whereas for the Feedyard C pond, the measurement locations were located more at distances greater than 60 feet (up to 400 feet) from the source.

The near field (close to source) over prediction by Ausplume (Figure 3) may be a function of the initial vertical spread (sigma z) as set by the user (0.5 m). The value was based on an initial height as to represent a source where the height of the cattle or the banks of the sedimentation basins will influence the initial vertical spread. The growth of the initial spread with fetch (plume growth with distance from the source) was not modeled in this exercise. Whilst it may be less of an issue with ponds, it could be significant with pens that have large fetches. The similarity between the pond and pen data in Figure 3 indicated that the increase in initial mixing height with distance across the source may not be very significant. Whilst the selection of the overall value of sigma z is likely to be the cause of the over prediction in the near field, adjusting this value is likely to exacerbate the under prediction in the far field. Future work is required in this area to further assess the reasons why the models differ when run for measurement points close to a source.

Conclusions

An assessment of emission rates derived using the Gaussian Ausplume and largangian WindTrax model indicated that the emissions rates derived using the models correlated well irrespective of the type of source (r^2>98%). Without direct measurements it is difficult to define which model provides the most accurate estimate of emissions. Work such as that of Sarkar and Hobbs (2003) and Galvin *et al.* (2004) has shown that dispersion models can correlate well with certain direct measurement techniques The models are inherently different and thus some difference was expected. Whilst the correlation between the two models was excellent there was consistent variation in the order of 20 % between the emissions predicted by the models and the theoretical 1:1 line. This did not appear to be a function of the size of the source. The data indicates that with sufficient knowledge of the models, the emission rate data derived using one model can be interchanged with the other models with confidence. Whilst not fully proven, it would appear that the way in which the models handle dispersion close to the source and thus distance to the source are important factors when back calculating emissions from area sources. To back calculate emissions from a source, a trade off may need to be made with respect to inaccuracies in the models near the source and the ability of the measurement technique to measure the species in question as it dilutes with distance from the source.

Future work should further investigate the use of improved meteorological parameters and the selection of initial mixing heights for emissions derived close to areal sources. Additionally thought should be given to the location of the downwind sampling point.

Acknowledgements

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Monitoring System Design for the Southeastern Broiler Gaseous and Particulate Matter Air Emissions Monitoring Project

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Abstract

Monitoring of air emissions that will provide data representative of southeastern U.S. broiler operations to the national Air Compliance Agreement is being conducted cooperatively by Iowa State University and The University of Kentucky. Two mechanically ventilated commercial broiler houses located in western Kentucky will be monitored for a period of one year. This study includes the quantification of building emissions for ammonia (NH_3), carbon dioxide (CO_2), hydrogen sulfide (H_2S), non-methane hydrocarbons (NMHC), total suspended particulates (TSP), particulate matter less than 10 microns in diameter (PM_{10}) and particulate matter less than 2.5 microns diameter ($PM_{2.5}$). This paper describes the continuous air pollutant monitoring system developed for use in this study. Two mobile air emission monitoring units were designed and fabricated at Iowa State University during the summer of 2005. Monitoring system installation was completed in fall 2005, and monitoring for all pollutants was initiated in January 2006. The mobile air emission monitoring units include a system to quantify pollutant concentrations within the broiler houses and a system to quantify the volume of air exhausted from each broiler house by the ventilation fans. Ammonia and carbon dioxide concentrations are measured using INNOVA 1412 photoacoustic multi-gas monitors. Hydrogen sulfide concentrations are measured using Teledyne API 101E pulsed fluorescence analyzers. Non-methane hydrocarbons are measured using a VIG-200 gas chromatograph and INNOVA 1412 photoacoustic multi-gas monitors. All three types of particulate matter are measured using TEOMs. Continuous measurement of air flow from each house is accomplished by measuring both building static pressure and the operational status of each ventilation fan. The fan operation status in conjunction with building static pressure were applied to in situ calibration fan curves developed for each fan using FANS units built at the University of Kentucky. Compact Field Point data acquisition hardware was utilized in conjunction with a custom data acquisition program written in Labview 7. Details of the monitoring system components is outlined in this paper.

Introduction

Accurate quantification of pollutant emissions from AFOs including commercial broiler production systems are needed to develop improved emissions inventories and emission factors for AFOs, as well as to determine if certain regulatory reporting requirements of emissions are required. A concern for the US poultry industry as well as for regulatory agencies is to ensure that reasonable estimates of emissions from broiler production systems are used. Currently, estimates based on continuous emission data for multiple air pollutants are lacking for these systems. The mass of a pollutant emitted from a facility is the product of source concentration of a pollutant and the air exchange rate through the source following proper unit conversions and correction for temperature and barometric pressure effects. It is a challenge to reliably quantify pollutant concentration and airflow in broiler production housing on a continuous basis. The use of intermittent ventilation by cycling of the ventilation fans off and on, especially when the birds are young, makes it necessary to correlate the in-house pollutant concentrations to the periods of fan operation in order to calculate emissions that are representative of those exhausted from the production housing. The pollutants of interest in this study include ammonia (NH_3), carbon dioxide (CO_2), total suspended particulate matter (TSP), particulate matter 10 microns or less (PM_{10}), particulate matter 2.5 microns or less ($PM_{2.5}$), hydrogen sulfide (H_2S) and non-methane hydrocarbons (NMHC). This project will quantify emissions from two commercial broiler production houses over a one year measurement period. Data from this project will be used to represent air emissions from southeastern U.S. broiler houses in the Air Quality Compliance Agreement (ACA), which will have regulatory significance to future enforcement and decisions made by the EPA in regards to air emissions from animal agriculture. Instrument selection for each pollutant of interest is shown in Table 1.

Pollutant	Monitoring Instrument
NH_3	Innova 1412, Innova AirTech Instruments A/S, Denmark
CO_2	Innova 1412, Innova AirTech Instruments A/S, Denmark
H_2S	UV Fluorescence Hydrogen Sulfide Analyzer Model 101E, Advance Pollution Instrumentation, San Diego, California
NMHC	Model 200 Heated Methane/Non-Methane/Total Hydrocarbon Analyzer, VIG Industries, Anaheim, California
NMHC	Innova 1412, Innova AirTech Instruments A/S, Denmark
TSP	Tapered Element Oscillating Microbalance (TEOM) Series 1400a with TSP inlet head, Thermo Electron Corporation, East Greenbush, New York
PM_{10}	PM_{10} - Tapered Element Oscillating Microbalance (TEOM) Series 1400a with PM_{10} inlet head, Thermo Electron Corporation, East Greenbush, New York
$PM_{2.5}$	$PM_{2.5}$ - Tapered Element Oscillating Microbalance (TEOM) Series 1400a with PM_{10} inlet head in conjunction with a 2.5 micron cut cyclone, Thermo Electron Corporation, East Greenbush, New York

Table 1. Monitoring Equipment Selection by Pollutant of Concern

Project Description

Two broiler houses associated with Tyson Foods broiler operations in Western Kentucky will be monitored in this extensive field monitoring study. The monitored broiler production houses use tunnel ventilation and box air inlets along the sidewalls which is representative of typical southeastern U.S. broiler production practices in terms of housing style and production management

Each broiler house has its own environment-controlled Mobile Air Emissions Monitoring Unit (MAEMU) that houses air pollutant and fan flow monitoring systems and provides an environment-controlled instrument area as shown in Figures 1 and 2. Air samples from the house sampling points (representing the exhaust air streams) to the MAEMU will be protected against in-line moisture condensation with insulation and temperature-controlled resistive heating cable. Building airflow will also be monitored continuously. A real-time data acquisition (DAC) program developed using LabVIEW 7 software (National Instruments, Corporation, Austin, TX) is used to acquire data, automate sampling location control, display real-time data, and deliver data and system operation status as shown in Figure 2.

Each MAEMU will house a gas sampling system, gas analyzers, environment-monitoring analyzers, a computer, DAC system, and other equipment needed for the study (Figure 3). Each broiler building will be sampled continuously for 12 months. The 12-month duration assures this project will meet the objectives of characterizing long-term emissions and to respond accurately to the need for annual emission factors from animal facilities by regulatory agencies and others. Long-term measurements allow the recording of variations in emissions due to seasonal effects, animal growth cycles, and diurnal variations. The two broiler houses, each 13.1m x 155.5m (43 x 510 ft) will be monitored at two different sites, 40 miles apart. The houses use four 91-cm (36-in) diameter sidewall exhaust fans spaced about 120 ft apart, and ten 123-cm (48-in) diameter tunnel fans for ventilation.

Figure 1. The Mobile Air Emissions Monitoring Unit (MAEMU).

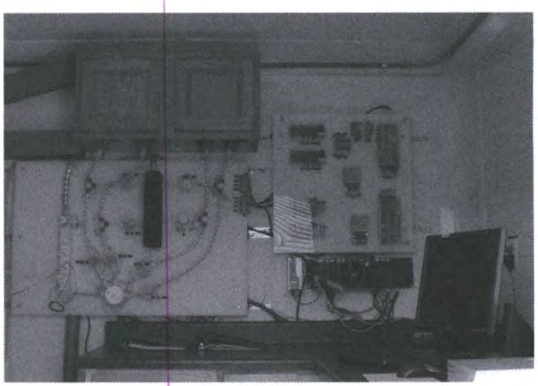

Figure 2. MAEMU Gas Sampling System Control System.

Experimental Design

The use of intermittent ventilation by cycling of the single-speed fans off and on, especially when the birds are young, makes it necessary to correlate the in-house pollutant concentrations to the periods of fan operation in order to calculate emissions that are representative of those exhausted from the production housing. Broiler house minimum ventilation exhaust fans are typically operated in five minute duty-cycles with a 30 second minimum run-time. For example, a fan could operate for two minutes and then turn off for three minutes during a five minute duty-cycle. Higher stage ventilation fan operation is based on temperature set points, which still results in intermittent fan operation. The determination of ventilation rates through the animal housing, based on manufacture supplied fan performance curves, is difficult due to the large number of fans involved and the inherent variation among them. As such, each fan is calibrated in situ to reflect the actual operating conditions in the field. For in situ calibration, the FANS method is used (Gates et al., 2004). During FANS testing, the fans operation status is tracked in conjunction with building static pressure to develop fan curves for each unit.

Air samples are drawn from three locations in each house (Figure 5), as well as from an outside location to provide ambient background data. One is located near the primary minimum ventilation (36-in) sidewall fan (SW1) used for cold weather ventilation (in the brooding half of the house). The second sampling location is near the fourth sidewall (36-in) exhaust fan (SW4) (non-brooding end). The third location is at the tunnel end for the first and higher stage of tunnel ventilation mode. In addition, an ambient air sample from outside the broiler house, near the eave between inlet boxes on the house sidewall that does not have exhaust fans will be taken at 2-hour intervals to provide a background concentration level. The background quantity will be subtracted from the exhaust quantity in calculating the pollutant emissions from each house. Air samples will be collected via 0.95-cm (3/8-inch) o.d. and 0.64-cm (¼-inch) i.d. teflon tubing (Fluorotherm FEP tubing). Sampling locations and placement of the sampling ports were chosen to maximize representation of the air leaving the houses. Each sample inlet point will be equipped with two paper pleated dust filters to keep large particulate matter from plugging the sample tubing as well as a 20 micron teflon filter to remove smaller particulate matter (Figure 4).

Individual supply pumps (with all internal wetted parts teflon coated) are used to continuously draw air from each of the sampling locations. The sampling train is designed such that a sample will be drawn from all four sampling points continuously and when a sample point is not being analyzed the flow will be bypassed at the instrument trailer. This arrangement is designed to minimize the residence time and thus greatly reduce sample-to-sample purging time. When analyzing each of the in-house air samples, four 30-second measurement cycles by the multi-gas (NH_3, CO_2, H_2O, and NMHC) analyzer will be performed to ensure attainment of 97% or better of the actual gas concentration values. Minimum time interval between samples is experienced when all fans are operational at all three sampling locations. This minimum time interval of a complete sampling cycle will be 360 s (120 x 3 = 360 s). To account for potential concentration changes during this period, linear interpolation between the two adjacent readings of the same location will be performed to determine the concentrations in between. If SW4 and/or TF1 fans are not operating, their sample analysis will be skipped, and the sampling will return to SW1 or fresh/background air. Airflow rates corresponding to the measured concentrations will be used in the calculation of the overall house emission rate. Since compositions of the background air are much more stable than the house air, the background will be sampled once every 2 hours. Due to the larger step change in ammonia concentration between the in-house air and background air, a longer sampling time (i.e. 5 minutes) will be used to allow full stabilization of the analyzer readings. Only the concentration readings at the end of the sampling cycle will be considered as valid measurements.

Figure 3. Gaseous emission monitoring instruments in MAEMU.

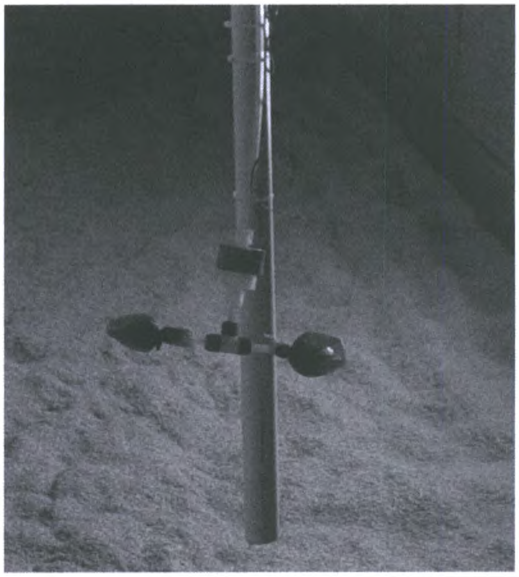

Figure 4. Gaseous emission in-house sample intake line with filters.

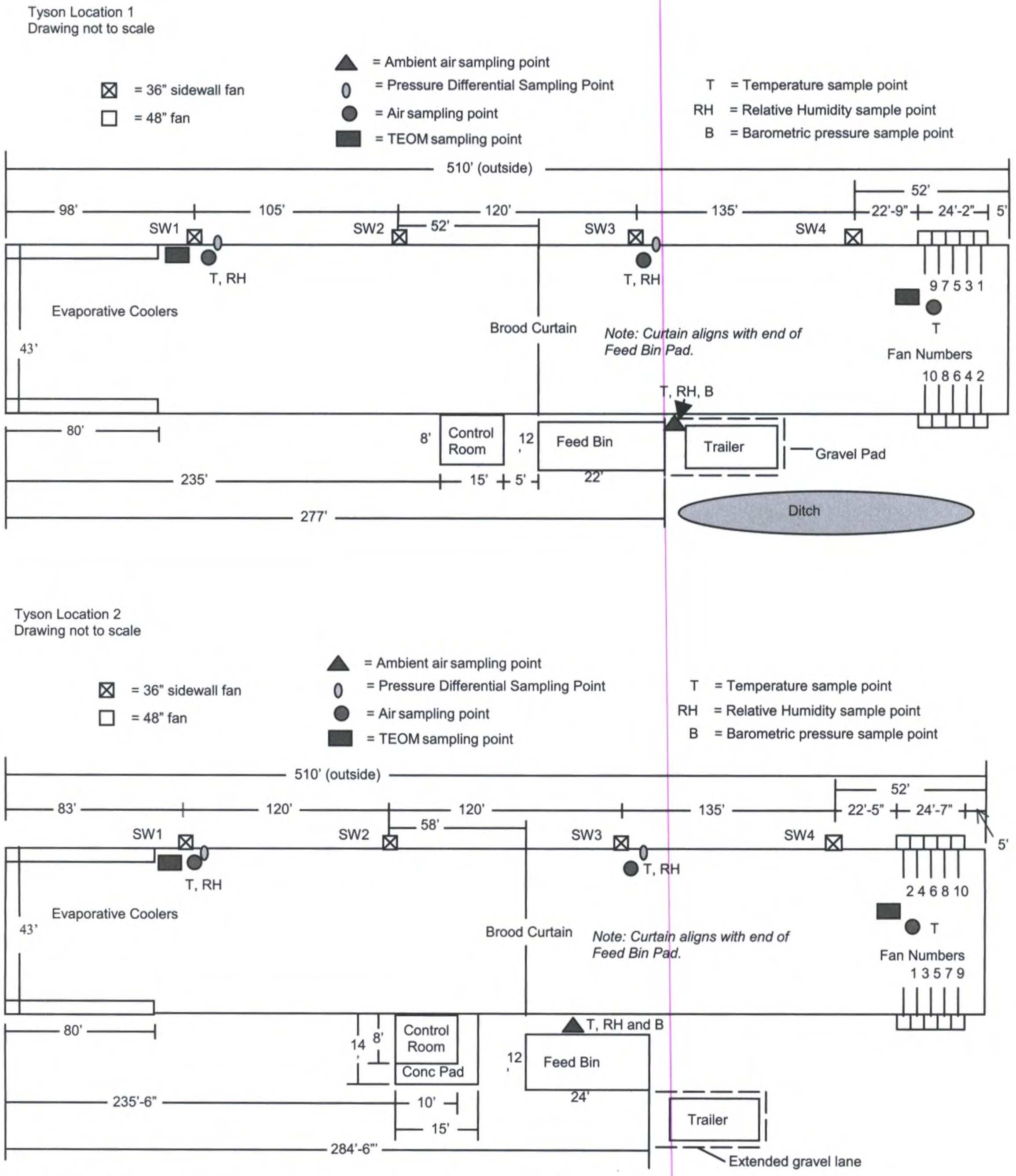

Figure 5. Schematic layout of Tyson Location 1 and 2.

Figure 6 shows the TEOMs in place inside the broiler facility. Placement of the TSP, PM_{10}, $PM_{2.5}$ TEOMs is as follows: while the brooder curtain is closed all TEOMs are places adjacent to the sidewall 1 fan. When the brooder curtain is opened the TEOMs will be relocated to the tunnel end of the house as shown in Figure 5. TEOM sampler location was determined following collection of dust concentration and air velocity data near the SW1 and tunnel fans. This data was used to identify areas where dust concentrations were representative of the concentrations being exhausted through the sidewall and tunnel fans.

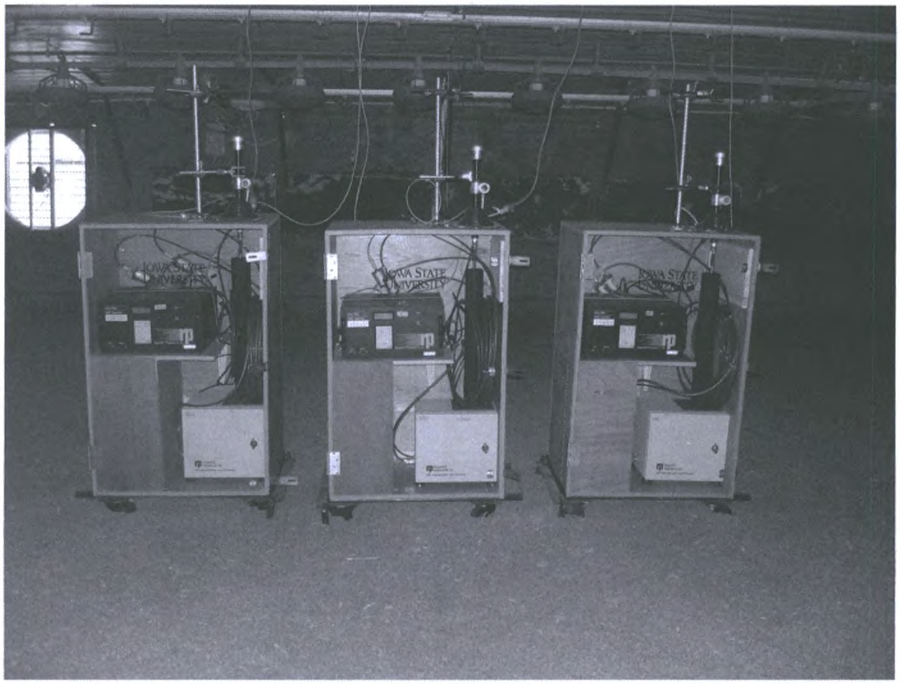

Figure 6. In-house particulate matter monitoring instruments for PM_{10}, $PM_{2.5}$, and TSP.

Summary

The main objective of this study is to determine and report emissions of ammonia (NH_3), carbon dioxide (CO_2), total suspended particulates (TSP), particulate matter 10 microns or less (PM_{10}), particulate matter 2.5 microns or less ($PM_{2.5}$), hydrogen sulfide (H_2S) and non-methane hydrocarbons (NMHC) based on continuous pollutant concentration and fan flow data over a one year period from broiler houses representative of commercial broiler production in the Southeastern United States. A primary concern for this study has been the establishment of reliable and accurate methods for determining contaminant concentration and ventilation rates in the environment of a broiler house for emission rate determination. Initial instrumentation and method testing began in the 3rd Quarter of 2005. Data collection began in the 1st quarter of 2006 and will conclude at the end of the 1st quarter of 2007. Results will be reported during the 3rd quarter of 2007. Because the harsh nature of the sample air, high humidity and high concentrations of the pollutants is beyond the operational limits of most analytical instruments, it is a challenge to reliably quantify concentration and airflow in animal production housing on a continuous basis (Xin et al., 2003). As the project representing the southeastern U.S. broilers in the Air Quality Compliance Agreement, extreme caution is being taken to obtain the most representative and highest quality data.

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Quality Assurance Project Plan (QAPP) Implementation for the Southeastern Broiler Gaseous and Particulate Matter Air Emissions Monitoring Project

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Abstract

Air emissions monitoring that will provide data representative of southeastern broiler operations to the national Air Compliance Agreement is being conducted cooperatively by Iowa State University and The University of Kentucky. Monitoring system installation was completed in fall 2005, and monitoring for all pollutants was initiated in January 2006 at two mechanically ventilated commercial broiler houses located in western Kentucky. The aerial emissions from the broiler houses quantified in this study include ammonia (NH_3), carbon dioxide (CO_2), hydrogen sulfide (H_2S), non-methane hydrocarbons (NMHC), total suspended particulates (TSP), particulate matter of $\leq 10\ \mu m$ diameter (PM_{10}), and particulate matter of $\leq 2.5\ \mu m$ diameter ($PM_{2.5}$). This paper describes the Quality Assurance Project Plan (QAPP) developed and implemented for this study, including the key components of Project Management, Data Generation and Acquisition, Assessment and Oversight, and Data Validation and Usability.

Introduction

In January 2005, the US Environmental Protection Agency (EPA) announced a plan, after negotiating with representatives of the animal agricultural industry, to collect scientifically credible data concerning air emissions from livestock and poultry facilities. This effort is titled the Air Compliance Agreement (ACA) (Copeland, 2005). Monitoring work performed as part of the ACA will have regulatory significance to future enforcement and decisions made by the EPA in regards to air emissions from animal agriculture. As such, projects within the ACA are required to operate with a Category 1 Quality Assurance Project Plan (QAPP) (US EPA, 2001).

The QAPP as defined by the EPA is a tool for project managers and planners to define the type and quality of data needed for environmental decisions, and to describe the methods for collecting and assessing those data. The QAPP integrates technical and quality control aspects regarding planning, implementation, and assessment for a project. The goal is to insure that the results of a project are of the type and quality needed and expected by the EPA. The four components of the plan are Project Management, Date Generation and Acquisition, Assessment and Oversight, and Data Validation and Usability (US EPA, 2001).

In the fall of 2005, Iowa State University and The University of Kentucky began implementing the first segment of the ACA monitoring for broiler operations. This segment of the study will monitor air emissions from two mechanically ventilated commercial broiler houses in western Kentucky. The study includes the quantification of emissions of ammonia (NH_3), carbon dioxide (CO_2), hydrogen sulfide (H_2S), non-methane hydrocarbons (NMHC), total suspended particulates (TSP), particulate matter of $\leq 10\ \mu m$ diameter (PM_{10}) and particulate matter of $\leq 2.5\ \mu m$ diameter ($PM_{2.5}$) from the broiler production facilities. The following section describes the development and implementation of key quality assurance and control components for the project's Category 1 QAPP as required by the EPA (US EPA, 2001).

QAPP Development and Implementation

Development and implementation of the QAPP for the Southeastern Broiler Gaseous and Particulate Matter Air Emissions Monitoring Project are discussed below by plan component.

Project Management

This component addresses the background and objectives for the project, the basic management of the project, and the responsibilities of the participants. All individuals participating in the project were identified and assigned tasks pertaining to their areas of expertise and participation level. Contact information for the participants was also included in this section. Project objectives and a brief summary describing the project were provided. A biosecurity plan was added to this component of the QAPP to outline the steps that should be taken by members of the project team when visiting the broiler facilities.

Data Generation and Acquisition

This component of the plan is key to identifying project design and steps for implementation. Methods identified here ensure appropriate methods for sampling, measurement and analysis, data collection, and quality control (US EPA, 2001). In the plan, this component clearly defines the experimental design, equipment selection and set-up, sampling methods, and quality control for our broiler air emission project.

As compared to air emissions monitoring for the commercial manufacturing and industrial sector, air emissions monitoring for agriculture is a more recent concern. Also, as compared to the industrial setting, monitoring of air emissions for agriculture is a small sector of the monitoring equipment economy. As such, while many types of analytical equipment and sampling methods are available, few have been standardized for agricultural situations. A primary concern for this study is the development of reliable and accurate methods for determining contaminant concentration and ventilation rates in the environment of a broiler house for the determination of pollutant emission rates. It is a challenge to reliably quantify concentration and airflow in animal production housing on a continuous basis (Xin et al., 2003). The harsh nature of the sample air, high humidity and high concentrations of the pollutants is beyond the operational limits of many analytical instruments.

Unique to broiler housing is the use of intermittent ventilation and thus operation of the (single-speed) fans, especially when the birds are young, to provide minimum ventilation, and at the same time has sufficient ventilation capacity to meet the needs of market-size birds under warm conditions. The use of intermittent ventilation by cycling of the (single-speed) fans off and on, especially when the birds are young, makes it necessary to correlate the in-house pollutant concentrations to the periods of fan operation in order to calculate emissions that are representative of those exhausted from the production housing. Broiler house minimum ventilation exhaust fans are typically operated in five minute duty-cycles with a 30 second minimum run-time. For example, a fan could operate for two minutes and then turn off for three minutes during a five minute duty-cycle. Higher stage ventilation fan operation is based on temperature set points, which still results in intermittent fan operation. This unique characteristic of building ventilation makes it necessary to correlate the in-house gas concentrations to the periods of fan operation in order to calculate emissions that are representative of those exhausted from the production housing. Consequently, the use of continuous, real-time analyzers with fast response times is critical for measuring emission concentrations from exhaust air in broiler houses. Two other critical issues for accurate emission rate calculation are location of sample intake within the facility and accurate determination of ventilation rates. The following is a list of analytical instruments selected for measurements of pollutant concentrations in this project.

- NH_3 – Innova 1412, Innova AirTech Instruments A/S, Denmark
- CO_2 - Innova 1412, Innova AirTech Instruments A/S, Denmark
- H_2S – UV Fluorescence Hydrogen Sulfide Analyzer Model 101E, Advance Pollution Instrumentation, San Diego, California
- NMHC – Model 200 Heated Methane/Non-Methane/Total Hydrocarbon Analyzer, VIG Industries, Anaheim, California , and Innova 1412, Innova AirTech Instruments A/S, Denmark
- TSP – Tapered Element Oscillating Microbalance (TEOM) Series 1400a with TSP inlet head, Thermo Electron Corporation, East Greenbush, New York
- PM_{10} - Tapered Element Oscillating Microbalance (TEOM) Series 1400a with PM_{10} inlet head, Thermo Electron Corporation, East Greenbush, New York
- $PM_{2.5}$ - Tapered Element Oscillating Microbalance (TEOM) Series 1400a with PM_{10} inlet head in conjunction with a 2.5 micron cut cyclone, Thermo Electron Corporation, East Greenbush, New York

After analytical instruments were selected for the project and prior to placement of each instrument at the monitoring sites, experiments were performed in the laboratory. Laboratory processing for all analytical instrumentation included initial calibration, verification and setting of analysis cycle time, assessment of dynamic response, accuracy and real-time interfacing with the data logging program and software. Prior to on-site analysis and data collection, field testing of the equipment was performed to ensure proper operation and placement.

For the gaseous emissions, four sample locations were identified, with three locations for in-house concentrations and one for outside ambient concentrations (Figure 1). Sampling from these locations is based on real-time fan operational status. For instance, if only one fan is operating then sampling repeats at that location, but if multiple fans are operating sampling will be sequenced repeatedly among locations. A sample line delivers the sample air from each location to the environmentally controlled Mobile Air Emissions Monitoring Unit (MAEMU) (Figure 2) where the instrumentation is housed and the air sample is split through a manifold to the three instruments.

Of particular importance for on-site testing was the determination of TEOM placement within the broiler house. Because the three TEOMs could not be placed at triplicate locations (due to budget limitations) as is the case with the gaseous sample lines, a best case placement was determined. Through on-site testing and air velocity profile measurements within the house, two locations were identified. During the brooding period, the TEOMs are placed beside sidewall fan 1 (SW1). When the brooding curtain is raised, the TEOMs are moved and placed near the tunnel end (Figure 1).

Accurate determination of ventilation rates is critical to proper calculation of air emission rates. Initially, all the exhaust fans were calibrated in situ, individually and in combined operation stages, with a Fan Assessment Numeration System (FANS) to obtain the actual fan performance curves (airflow rate vs. static pressure) (Gates et al., 2004). Once the actual airflow curves are established for all the exhaust fans and their combinations, runtime of each fan is monitored and recorded continuously by sensing ON/OFF state of the current switches (CR9321, CR MAGNETICS, INC, St. Louis, MO) driven by the current flow through the fan power supply cord. Concurrent measurement of the house static pressure is made with differential pressure sensors (Model 264, Setra, Boxborough, MA). Summation of airflows from the individual fans during each monitoring cycle or sampling interval yields the overall house ventilation rate. This method of determining dynamic ventilation rates of mechanically ventilated animal confinement has been successfully used in recent AFO air emission studies in the United States (Gates et al., 2005, Wheeler et al., 2006).

In addition to describing the steps taken to implement the project and verifying accuracy of the results, this component of the QAPP also provides explicit details for project duration quality control. Recalibration triggers and schedules are described. Moreover, standard operating procedures (SOPs) for handling all instruments and systems components are included as Appendices.

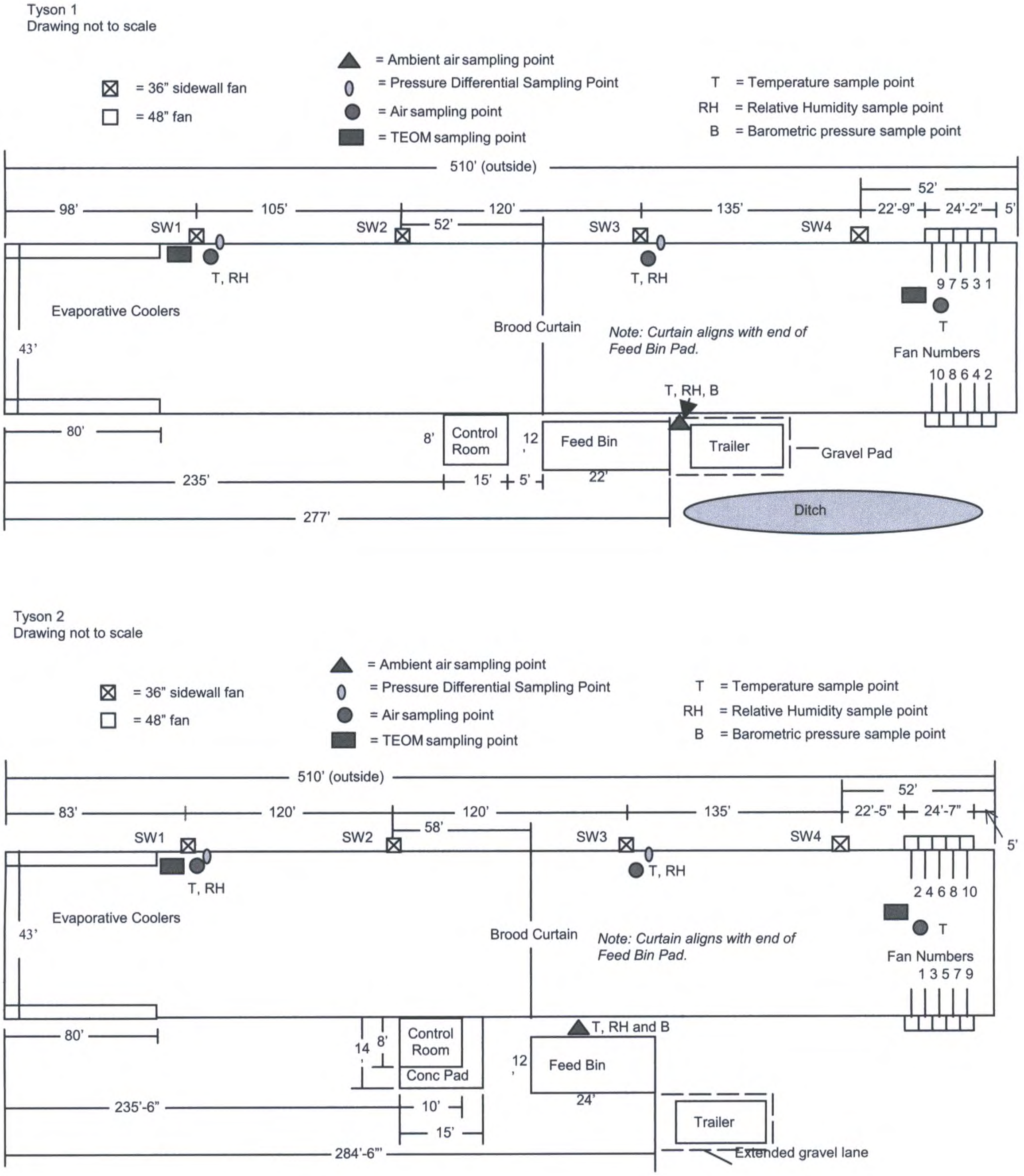

Figure 1. Schematic layout of Tyson 1 and Tyson 2.

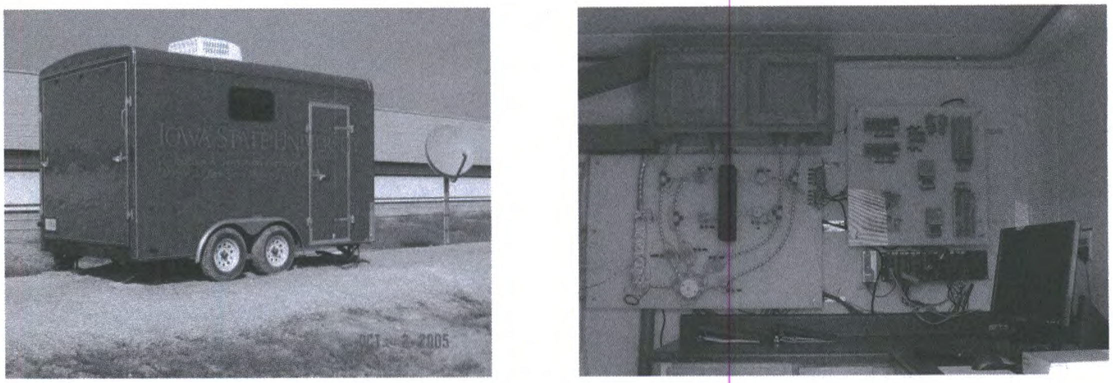

Figure 2. Inside and outside views of the Mobile Air Emissions Monitoring Unit (MAEMU).

Assessment and Oversight

This section of the plan addresses the required activities for assessing the effectiveness of the quality assurance and quality control activities associated with implementing the plan. A combination of remote surveillance, on-site surveillance, internal technical systems audits, external technical systems audits and out of range data flagging/review is used to provide project assessment.

Remote surveillance is conducted on a daily basis via a high-speed internet connection to each MAEMU. Using a web-based remote interface, all pollutant monitoring readings can be viewed in real time as well as individual fan operational status, pressure differential, temperature, relative humidity and dew point conditions at all four sampling points. A complete on-site surveillance of the monitoring system is conducted weekly at each monitoring site. During weekly visits to each site project personnel perform a visual check on all system components including in-house sampling points, TEOMs and fans, the ambient monitoring point, and all instruments and components located inside the MAEMUs. During this visit paper element filters and the 20 micron teflon filters are replaced, and the TSP, PM_{10} and $PM_{2.5}$ TEOM heads are exchanged for clean heads (TEOM heads are exchanged twice per week due to the high dust conditions encountered in the broiler houses). A report detailing assessment observations and any required response actions is prepared following the visit and emailed to team members.

Internal technical system audits are performed between flocks. The broiler houses are empty for approximately ten days following the removal of each flock of birds. During this ten day period, ISU and UK project personnel conduct an internal technical systems audit at both monitoring sites. This audit includes a visual inspection of all system component, and a flow check at each of the four sample points to confirm pump flows are maintaining a 15 liter per minute flowrate. A flow-audit is conducted on each TEOM during the audit. Leak checks of the GSS and supply lines are conducted by calibrating an additional INNOVA 1412 with the INNOVA 1412 located in the MAEMU and then placing the second INNOVA 1412 at each sample point inside the broiler house and confirming matching ammonia readings. This provides a confirmation that no dilution air is entering the system, and thus that no leaks are present.

An external technical systems audit team has been established and will conduct an audit following acceptance of the project QAPP. The audit team members are nationally recognized experts in AFO air emissions monitoring who have no association with the project. The external auditors will make a visit to each site and will include a review of calibration and QC measures.

All data will be reviewed for out of range data using a computer program. The data processing program automatically flags out of range data and project personnel will review flagged data on a weekly basis and confirm that the data is invalid, or override the flag if data is determined to be valid. Flagged data will not be used in emissions calculations. A record of data review and any removal of data following review will be maintained. The response action to data flagged as out of range will be to investigate and document the reason that the data was flagged and to follow-up with a site visit if any data flags were the result of equipment malfunction and correct the problem.

Data Validation and Usability

This component describes the activities that occur after the data collection phase of the project. Because this project involves a long period of intensive data collection, steps for continuous review and validation of the data are necessary. To improve the ease with which data are reviewed, real-time emission calculations are performed on site by the PC as data are collected and recorded. However, all raw data are also recorded. All data are reviewed within two business days after having been recorded.

Summary

While a requirement for this project, development of a detailed Quality Assurance Project Plan (QAPP) is a very useful planning tool when implementing and managing projects of this size and importance. The US EPA provides in depth descriptions of what is necessary for a QAPP. Addressing the four plan components (Project Management, Date Generation and Acquisition, Assessment and Oversight, and Data Validation and Usability) will ensure that the results of a project are of the type and quality needed and expected. The team participating in the western Kentucky broiler house air emissions monitoring feels that the steps detailed in the project's QAPP are conducive to assuring the quality of the methods and results.

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Measurement, Analysis, and Modeling of Inorganic Fine Particulate Matter in Rural, Ammonia-Rich Areas in Eastern North Carolina

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Abstract

Gaseous emissions of ammonia from confined animal feeding operations (CAFOs) in eastern North Carolina have become an environmental issue of concern. These emissions cause an impact in eastern North Carolina in many different ways such as human health, and increased fine particulate formation on a local and regional scales. To study these impacts, acidic gases and inorganic fine particulate matter ($PM_{2.5}$) concentrations were measured at a hog farm in eastern North Carolina, and at a down wind site ~10 miles away. This analysis showed slight seasonal differences in both gas and PM concentrations and the insights into the gas/particulate interface. To study the regional impact, an analysis of fine particulate data in eastern North Carolina was conducted in order to investigate the impact of the hog industry and its emissions of ammonia into the atmosphere. This fine particulate data is simulated using ISORROPIA, a thermodynamic model that simulates the gas and aerosol equilibrium of inorganic atmospheric species. The observational data analyses show that the major constituents of fine PM are organic carbon, sulfate, and ammonium, nitrate, and elemental carbon. The observed $PM_{2.5}$ concentrations ares positively correlated with temperatures but anti-correlated with wind speeds. The correlation between $PM_{2.5}$ and wind direction at some locations indicates the impact of the emissions from hog facilities on $PM_{2.5}$ formation. The modeled results are overall in good agreement with observations, with slight better agreement at urban sites than at rural sites. The predicted total inorganic PM concentrations are within 5% of the observed values under conditions with median initial total PM species concentrations, median RHs, and median temperatures. The ambient conditions with high PM precursor concentrations, low temperature, and high relative humidity favor the formation of the secondary PM.

A PM_{10} Emission Factor for Free Stall Dairies

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Abstract

Ambient concentration measurements of total suspended particulate (TSP) were made at a commercial dairy in central Texas during the summers of 2002 and 2003. The facility consisted of both open pen housing and free-stall structures to accommodate approximately 1840 head of milking cows. The field sampling results were used in the EPA approved dispersion model Industrial Source Complex Short Term version 3 (ISCST-v3) to estimate emission fluxes and ultimately develop a seasonally corrected emission factor for a free stall dairy.

Ambient measurements of TSP concentrations for sampling periods ranging from 2 to 6 hours were recorded during the summer of 2002. The mean upwind concentration was $115\mu g/m^3$ with a maximum of $231\mu g/m^3$ and a minimum of $41.4\mu g/m^3$. The mean net downwind TSP concentration was $134\mu g/m^3$ with a maximum of $491\mu g/m^3$ and a minimum of $14\mu g/m^3$. Field sampling at this same dairy in the summer of 2003 yielded significantly more 2 to 6 hour TSP concentration measurements. The mean upwind TSP concentration was $76\mu g/m^3$ with a maximum concentration of $154\mu g/m^3$ and a minimum of $36\mu g/m^3$. The mean net downwind TSP concentration was $118\mu g/m^3$ with a maximum of $392\mu g/m^3$ and a minimum of $30\mu g/m^3$.

The particle size distributions (PSD) of the PM on the downwind TSP filters was heavily influenced by the PSD of PM upwind of the dairy source. This is a consequence of the relatively low PM concentrations downwind versus upwind. The respective mass of PM in the different size ranges utilizing the upwind PSD and measured concentrations were subtracted from corresponding mass of the downwind PSD and measured concentrations, and were used to produce a net PSD that is attributed to the source. The result of this process was a representative dairy PM PSD. The mathematical representation of the dairy PSD is a lognormal distribution with a mass median diameter (MMD) of 15µm and a geometric standard deviation of 2.1. With this dairy PSD, PM_{10} concentrations can be determined from a measured TSP concentration by multiplying by 0.28. In other words, the average percent mass of TSP emitted by dairies corresponding to PM_{10} is 28%.

The reported PM_{10} 24-hour emission factors were 5.0 kg/1000hd/day for the free stall areas of the facility and 15 kg/1000hd/day for the open pen areas of the dairy. These emission factors were uncorrected for rainfall events. Corrections for seasonal dust suppression events were made for the San Joaquin Valley of California and the panhandle region of Texas. Using historical rainfall and ET data for central California, the seasonally corrected PM_{10} emission factor is 5.0 kg/1000hd/day for the free stalls, and 11.2kg/1000hd/day for the open pens. For Texas, the seasonally corrected emission factors are 5.0 kg/1000hd/day for the free stall areas and 11.3 kg/1000hd/day for the open pens.

Unlike cattle spacing on cattle feedyards, the dairy cattle spacing is significantly different for the open lot areas versus free-stall areas. Using a free stall spacing of 9.29square meters per cow (m^2/cow) located in the free stall area and $46.5m^2$/cow located in the open lot area fluxes can be calculated and/or emission factors can be calculated. The seasonally corrected PM_{10} emission factors for California of 5.0kg/1000hd/day for the free stalls, and 11.2kg/1000hd/day for the open pens correspond to fluxes of $6.2\mu g/m^2/s$ and $2.8\mu g/m^2/s$ for free-stall and open lot areas, respectively. The seasonally corrected emission factors for a Central Texas Dairy are 5.0kg/1000hd/day for the free stall areas and 11.3 kg/1000hd/day for the open lot areas corresponding to fluxes of $6.2\mu g/m^2/s$ and $2.8\mu g/m^2/s$ for free-stall and open lot areas, respectively.

These emission factors represent drastic reductions from those used by many regulatory agencies. The past emission factors attributed to dairies were reported to be as high as 61.4 kg/1000hd/day PM_{10}. This is due to the historical use of the former AP-42 beef feed yard emission factor as a starting point for determining dairy emissions. Due to the numerous errors in the development of the former AP-42 beef feed yard emission factor and the drastic differences between the dairy and beef facilities, it is not appropriate to use that emission factor for dairies. This work clearly displays that not only it is correct in theory but actual field sampling and emission factor development also showed that adapting a beef feed yard emission factor for use on dairies is a gross misuse of AP-42 emission factors.

Update on the National Air Emissions Monitoring Study

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Abstract

The National Air Emissions Monitoring Study is designed to provide quality-assured air emission data from representative swine, egg layer, dairy and broiler production facilities in the U.S. Following sound scientific principles and using accepted instrumentation and methods, this project will collect new data from 10 to 25 farms across the country to form a database to which additional studies of air emissions and effectiveness of control technologies can be compared. These benchmark data and accompanying analysis and interpretation will allow U.S. EPA and livestock and poultry producers to reasonably determine which farms are subject to the regulatory provisions of the Clean Air Act and reporting requirements of CERCLA and EPCRA. The study involves air emissions from both barns and open waste storage facilities over a two-year period—capturing the variation in emissions with time of year, stability of the atmosphere, and changes in facility operation. Gaseous emissions (NH_3, H_2S, some VOCs) from open waste storage facilities (lagoons and waste basins) and open feedlots will be made at many farms using open path optical remote sensing in conjunction with micrometeorological measurements and various plume modeling techniques. Gaseous and aerosol emissions (NH_3, NO_X, H_2S, CO_2, total VOCs, TSP, PM_{10} and $PM_{2.5}$) from barns at many farms of varying character will be determined by measuring exhaust concentrations and airflow while closely monitoring internal processes.

Vegetation Management and Competition in Future Ozone Climates

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Abstract

Vegetation management to reduce crop-weed competition in agroecosystems is heavily reliant on non-renewable energy for cultivation and/or synthetic chemicals. Both have air quality implications in direct proportion to the magnitude of infestation and the difficulty of controlling the competing weed species. The magnitude of weed infestation is a function of competition with the crop itself, and of biotic and abiotic environmental conditions, including air quality. The difficulty of controlling a weedy species, in many modern production systems, may be a simple function of its resistance to herbicides. The present work considers the potential interaction between rising concentrations of tropospheric ozone and (1) the competitive interactions between common crops such as cotton and tomato with weeds such as nightshade (*Solanum nigrum*) and nutsedge (*Cyperus esculentus*). We have investigated these interactions across a range of exposures to ozone. Exposures have been administered in field exposure chambers. In the case of cotton or tomato competition with yellow nutsedge, competitive outcomes in vegetative plants were predicted by the relative sensitivities of the pairs of species. In the case of cotton and nightshade, both crop and weed were sensitive to ozone but the combined impact of weed pressure and ozone resulted in the near elimination of cotton from the combined system. We conclude that ongoing climate change, including increasing tropospheric ozone concentration, will alter best management practices for common weeds in many cropping systems. In many cases additional vegetation management interventions will be required to maintain current yields. In addition to these direct effects, the changes will also have indirect effects on air quality, increasing emissions of NO_x and VOC from vehicles involved in the additional cultivation procedures and emissions of VOC from the applied herbicides.

Introduction

The San Joaquin Valley of California (SJV) is a highly productive agricultural region in which crops absorb considerable O_3 from the atmosphere (Grantz et al., 1994). As a consequence, yields of cotton (*Gossypium spp.*) and tomato (*Lycopersicon esculentum* Mill.) are reduced substantially (Brewer et al., 1986; Oshima et al., 1979; Temple et al., 1985, 1988), particularly cultivars of long-staple Pima cotton (*G. barbadense* L.) selected elsewhere (Olszyk et al., 1993). The older Pima cultivar, S-6, exhibits considerable physiological and yield sensitivity to current ambient concentrations of O_3 (Grantz, 2003; Grantz and Yang, 1996, 2000; Grantz et al., 2003), with yield losses approaching 20% (Olszyk et al., 1993), though recent cultivars selected in the SJV are reported to be more tolerant. Yield losses in tomato of over 24% were observed in the SJV in cv. 'Murrietta' (Temple et al., 1985).

Continued productivity of both cotton and tomatoes in the SJV is increasingly threatened by rising ambient concentrations of ozone. Ozone is increasing regionally and globally even as it declines in some urban areas (NARSTO, 2000).It appears to be an aspect of ongoing climate change that is likely to have substantial near-term impacts on native and cultivated vegetated systems (Davison and Barnes, 1998; Heck et al., 1988; Krupa et al., 2001; Lefohn, 1992; Fuhrer, 2003; Patterson, 1995).

In the SJV and elsewhere, economic crop production is also challenged by weed pressure. Weeds continue to account for substantial economic costs and crop yield losses globally (Buhler, 2003). Vegetation management is a major cost of production. Herbicide is applied to approximately 60% of the land area under cotton cultivation in the SJV (DPR, 2002), increasing yields by an estimated 2.5-fold (NCFAP, 2002). Herbicides are applied to 99% of the tomatoes grown in California, increasing yields by an estimated 20% (NCFAP, 2002).

Yellow nutsedge (*Cyperus esculentus* L.) is a particularly difficult weed to control, particularly in irrigated row and vegetable crops (Holm et al., 1991; Mulligan and Junkins, 1976). Yellow nutsedge reduces yield of tomatoes through both above- and below-ground competition (Morales-Payan et al., 2003). It is a major pest in cotton under irrigated SJV conditions. As a C_4 species, it is well adapted to hot, dry climates. Reproduction is largely or entirely by below ground production of vegetative tubers.

Black nightshade (*Solanum nigrum*) is a C_3 plant that has become a problem in both cotton and tomato in California (DeFelice, 2003), and in the presence of an established seed bank is quite difficult to control (Perez and Masiunas, 1990; Keeley and Thullen, 1991). It reproduces copiously by seed production, and exhibits canopy characteristics very similar to both crops, competing with both mainly for light interception.

While O_3 impacts on competitive interactions are potentially quite significant, little is known of interspecific interactions under elevated O_3 (Fuhrer and Booker, 2003; Ziska, 2002). The relative ozone tolerance of competing species may not predict competitive outcomes in the presence of O_3 exposure. Under open top chamber (OTC) exposure conditions, for example, blackberry (*Rubus cuneifolius*) came to dominate an early successional community previously dominated by sumac (*Rhus copallina*; Evans and Ashmore, 1992), despite the great sensitivity of blackberry to O_3. Grass-legume pasture communities (e.g. *Lolium perenne* L.-*Trifolium repens L., Festuca arundinacea-T. repens,* and *Phleum pratense* L.-*Medicago sativa* L.) have tended to simplify toward pure grass during O_3 fumigation in both open air and chamber facilities (Nussbaum et al., 1995; Rebbeck et al., 1988; Wilbourne et al., 1995; Johnson et al., 1996). The degraded performance of the legumes and increasing competitiveness of the grasses may be explained by O_3 inhibition of biomass allocation to storage roots of the former.

In many weedy species, short life cycles and prolific seed production and dispersal will accelerate adaptation to high ambient O_3 concentrations. In others, abundant production of reproductive vegetative tubers may limit the rate of such adaptation.

Methods

Competition experiments with yellow nutsedge and cotton or tomato were conducted in open top field exposure chambers (Heagle et al., 1973) at the University of California, Kearney Research and Extension Center, Parlier, CA. O_3 was generated by corona discharge from purified oxygen (Model G22; Pacific Ozone Technology, Brentwood, CA; Model AS-12; AirSep Corporation, Buffalo, NY), 24 hours per day, 7 days per week. The low O_3 regime was charcoal filtered, achieving approximate 12 hour mean exposures of 12 nL L^{-1}). The medium O_3 regime was charcoal filtered with O_3 added to approximate a local diurnal profile of a polluted day (Grantz et al., 2003), with nominal maxima of 140 nL L^{-1}. The high O_3 regime was 1.5-fold greater than the medium.

Juvenile individuals of yellow nutsedge (*Cyperus esculentus*; single tuber; shoot approximately 6 cm tall; 2-3 leaf blades) were collected in the eastern SJV and transplanted, cotton (*Gossypium barbadense*; cv. Pima S6; J.G. Boswell Co., Corcoran CA) was planted as seed, and tomato was obtained as 3 wk old nursery stock (15-cm tall; cv. HD 8892 or cv. EMP 113) and transplanted. Plants were grown in 9 L (45 cm deep x 18 cm diameter) polyethylene pots in 6-40 mesh sintered clay (Quicksorb, A & M Products, Taft, CA). Cotton or tomato were planted or thinned to one uniform plant pot^{-1} and nutsedge to 0, 1, 2, or 3 plants pot^{-1}. Additional pots contained single plants of nutsedge, alone. Pots were drip irrigated and well fertilized.

Competition experiments with black nightshade (seed collected in the western SJV) and cotton (*cvs.* Pima S6 and S7; data pooled) were performed in closed-top field exposure chambers (Musselman et.al., 1986) at the University of California, Riverside, CA. Chambers had teflon walls to reduce heat load and ozone reactivity. A range of ozone (O_3) concentrations was delivered to the chambers by mixing charcoal filtered air with unfiltered ambient air (Musselman et.al., 1986), with 100, 80, 60, 40, and 0 % ambient air, 24 hours per day, 7 days per week. 0% ambient chambers achieved approximately 25 nL L^{-1} 12-hr seasonal mean.

Plants were grown in the ground, which had been excavated and replaced with a uniform soil mixture(U.C.Soil Mix II) pre-fertilized with 82 g of 16-20-0 (equivalent to 28 kg N/ha). Seed of Pima cotton (cv. S-6) were spaced 0.076 m within rows and 0.75 m between rows oriented N-S. Seed of nightshade were planted within the row at 30 cm intervals. The crop was dominated by weeds in the first year and the planting was destroyed. Measurements were taken in the following year, when cotton was replanted and volunteer nightshade appeared at similar densities in all chambers. Plants were drip irrigated weekly.

O_3 exposures differed between experiments and repetitions within experiments. Averages (12 hour means across all reptitions) are indicated in the figures.

Results and Discussion

We use data from several systems to explore the possible effects on vegetation management of increasing ozone in rural areas. The cotton-nutsedge and tomato-nutsedge experiments have been described elsewhere (Grantz and Shrestha, 2006; Shrestha and Grantz, 2005). The cotton-nightshade experiments have not been described previously.

Black nightshade is an economically important weed in cotton and tomato, exhibiting a similar canopy morphology. At very high weed density it completely shaded out the cotton at all concentrations of ozone (not shown, data from the first year after planting). At the more moderate densities achieved in the subsequent year, cotton competed well, developing an approximately 6.8-fold superiority in shoot biomass over nutsedge at low ozone concentration (cf. Fig. 1B,C). At higher ozone concentrations, however, cotton was nearly out-competed, with its shoot biomass advantage reduced to about 2.7-fold. Total above ground biomass of the system was reduced by ozone by 41% (Fig. 1A), while nightshade biomass increased by 26% (Fig. 1B). This reflected the reduced competition, particularly for light, exherted by the cotton (Fig. 1C) as its shoot biomass declined by 49%.

In this study we do not have measurements of the ozone sensitivity of the two species grown alone. In the mixed system, the impact of ozone on this crop-weed system was to inhibit cotton directly, as shown in previous studies, and to creat a competitive opening which nightshade was able to exploit. Nightshade was not particularly tolerant of ozone. The main impact in future atrmospheres may be the increased competitiveness of nightshade and an increased seed bank following high ozone years due to this enhanced performance.

Yellow nutsedge is also an economically important weed in cotton and tomato, but one which does not exhibit a similar canopy and does not compete effectively with the crop for light. In cotton grown without competition (Fig. 2A), shoot biomass was reduced by ozone by about 25% at the near ambient ozone concentration and by about 75% at elevated ozone. In cotton grown with nutsedge competition, cotton biomass was reduced significantly by about 50% over all levels of nutsedge competition (Fig. 2A).

The presence of just one nutsedge plant (1:1) reduced shoot biomass of cotton at all levels of O_3 (Fig. 3A). The effects of ozone and nutsedge competition were additive, with an overall reduction at the highest ozone and with nutsedge competition (Fig. 2A) of 87% in shoot biomass productivity. This interaction was not significant, but the significant linear relationships at all levels of O_3 between 1/biomass and competition intensity (Passini, 2003) clearly distinguished the effect of competition at low and medium ozone from that at high ozone (Fig. 3B). Exposure to O_3 at the higher than ambient concentration altered the competitive interaction between cotton and nutsedge.

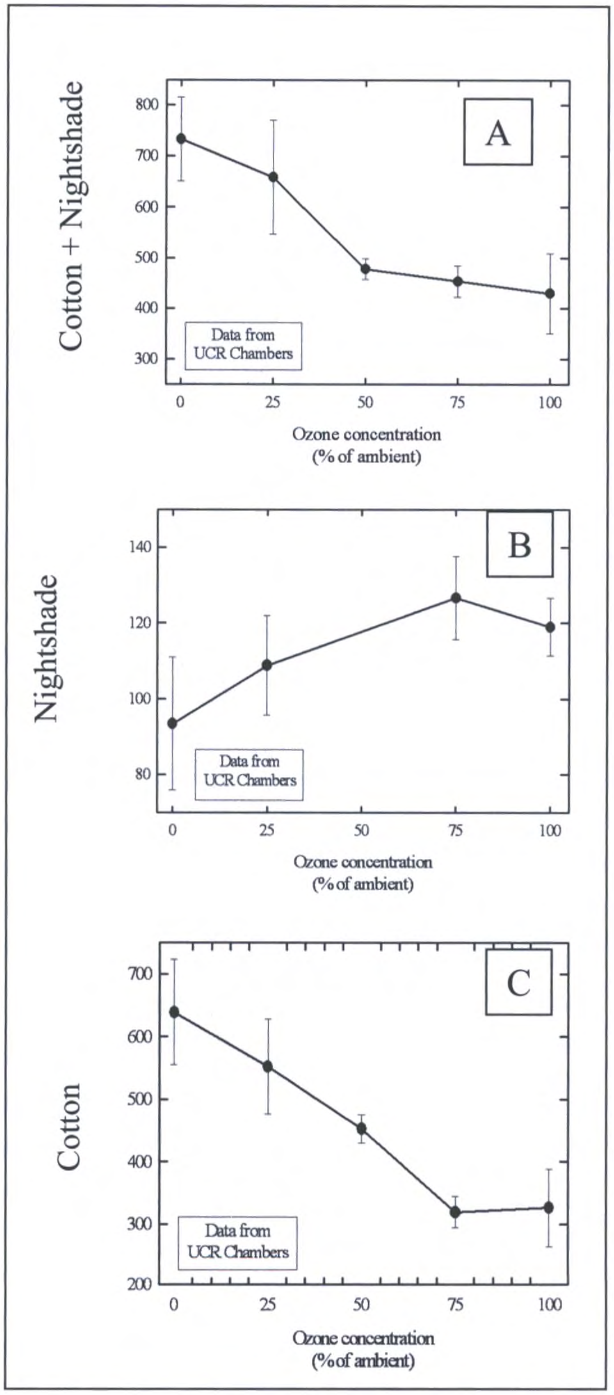

Figure 1. Competition between black nightshade and Pima cotton over a range of ozone exposures. Effect of ozone on shoot biomass (g/m row) of (A) both species pooled, B) nightshade, and (C) cotton.

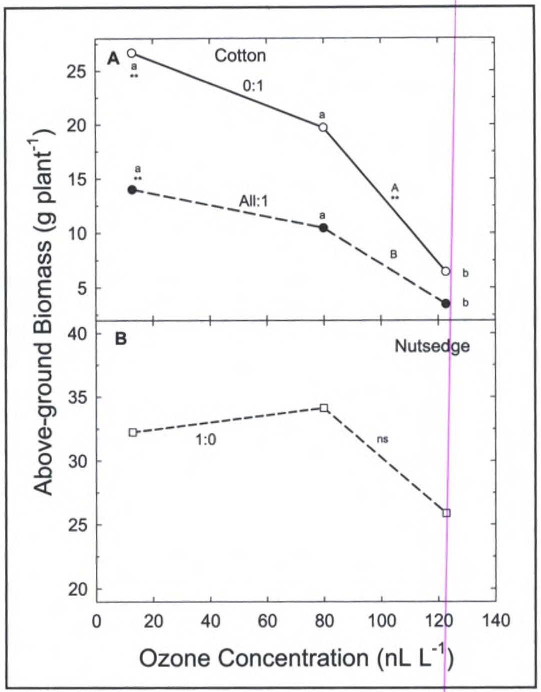

Figure 2. Effect of ozone exposure on above-ground biomass productivity of cotton (A) and nutsedge (B). Open symbols represent each species grown alone; closed symbols represent the average of all levels of nutsedge competition. Inset presents the effects of nutsedge competition on shoot growth at each level of O_3 exposure. Statistical differences between means within a line are indicated by different lower case letters and symbols indicating the level of significance. Statistical differences between lines are indicated by upper case letters.

In nutsedge grown alone (Fig. 2B), above-ground biomass (shoot minus rhizomes and tubers) was not significantly impacted by O_3, but consistently (cf. Fig. 2B, 5B) exhibited maximal shoot biomass at medium ozone and declined at high ozone by 24%.

Root production in cotton grown alone (Fig. 4A, circles) declined with increasing exposure of the shoot to O_3. At the highest ozone concentration root biomass was reduced by approximately 85%, similar to previous results (Grantz and Yang, 1996, 2000). The root:shoot (R:S) biomass ratio of cotton was reduced by O_3 exposure (not shown), particularly at high ozone relative to low and medium ozone, despite the large O_3-induced reduction observed in above ground biomass. Reduced allocation of photosynthate to sink tissues and the associated inhibition of root development are commonly observed following exposure to ozone (Cooley and Manning, 1987; Reiling and Davison, 1992; Grantz et al., 2006).

Reduced allocation to shoot tissues such as stolons (Wilbourn et al., 1995; Barnes et al., 1998) has also been observed following exposure to ozone. Below-ground biomass of nutsedge contains both shoot and root vegetative tissues as well as shoot-borne reproductive tubers. Nutsedge grown alone produced considerably greater below ground biomass than did cotton (Fig. 4A). The two root systems could not be separated quantitatively when grown together. The combined root biomass decreased with increasing O_3, and increased marginally with increasing nutsedge density. The two species inhibited each other to a similar extent below ground, since the 1:1 root mass fell midway between 0:1 and 1:0 (Fig. 4A; triangles), particularly at near ambient ozone.

Allocation below ground was not significantly affected by O_3 in nutsedge grown alone (Fig. 4A), though in our experiments it has consistently declined at medium (near ambient) ozone concentrations relative to clean air concentrations and recovered (often increased) at high ozone (cf. Fig. 6). The nearly opposing responses of above and below ground biomass (cf. Figs. 2B, 4A) resulted in a substantial reduction in the below:above-ground biomass ratio at medium ozone, but a complete recovery at high ozone (not shown). Total tubers per plant was generally maximal at medium ozone exposure (Fig. 4B).

In the tomato-yellow nutsedge system the presence of nutsedge (averaged across all population ratios) caused a decline in tomato shoot biomass over all O_3 concentrations imposed (Fig. 5A). Increasing O_3 concentrations also reduced shoot biomass of tomato, whether grown with or without nutsedge. In tomato grown alone, shoot biomass declined by 31% between low and medium ozone concentrations, but with little further reduction at elevated ozone (Fig. 5A, open circles).

Shoot biomass (above-ground excluding rhizomes and tubers) of nutsedge grown alone (1:0) increased at moderate ozone exposure (Fig. 5B), but declined significantly, by 42%, at high relative to medium ozone (Fig. 5B).

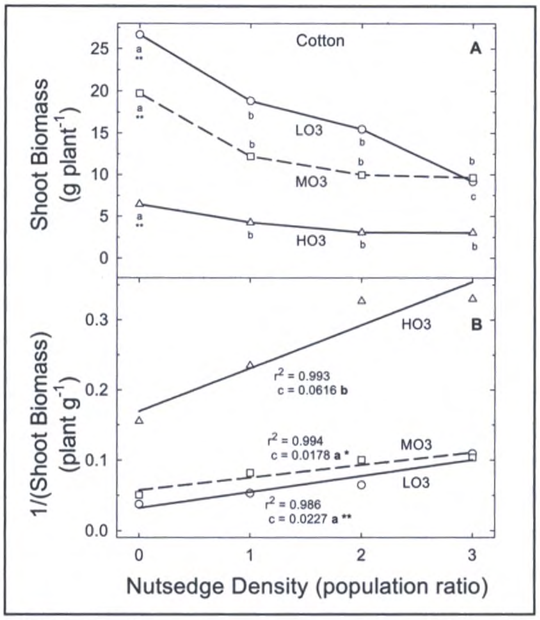

Figure 3. Effect of nutsedge density on shoot biomass (A) and on the inverse of shoot biomass (B) of cotton at each level of ozone exposure. In (B) the slope of each line is interpreted as a competition coefficient.

Shoot biomass of nutsedge was more impacted by tomato than it was by ozone (Fig. 5B). At each concentration of O_3, the addition of a single tomato plant to a nutsedge plant substantially reduced the shoot biomass of nutsedge (Fig. 5B). Even a 3:1 population advantage did not increase shoot biomass of nutsedge to the level observed in the absence of tomato competition (Fig. 5B). In previous studies (Morales-Payan et al., 2003) shoot production of nutsedge was reduced by 33% when grown in competition with a tomato plant. Our findings support the earlier conclusion (Santos et al., 1997) that nutsedge is a relatively weak inter-specific competitor (e.g. for light), but a strong intra-specific competitor.

Tomato root biomass declined nearly linearly with ozone concentration (Fig. 6; open circles). Root biomass was approximately 25% lower at MO3 and 44% lower at HO3, relative to LO3.

The effect of competition from nutsedge on tomato root biomass was difficult to evaluate, as it was for cotton, because the two root systems could not be separated quantitatively. The combined root biomass of tomato and nutsedge (grown at 1:1) was similar to that of tomato alone (0:1), but substantially less than that of nutsedge alone (1:0), at all concentrations of ozone. Thus, tomato inhibited nutsedge productivity more than nutsedge inhibited tomato. In previous studies, measurements of reduced-NO_3 in tomato sap when grown in the presence of nutsedge (Morales-Payan et al., 2003) indicated that significant competition between these species may take place belowground.

The root:shoot biomass ratio of tomato was reduced by O_3 concentration, particularly at high relative to low ozone concentration (not shown). This reflected the nearly balanced decline in both root and shoot biomass as O_3 exposure increased (Fig. 5A, 6; open circles).

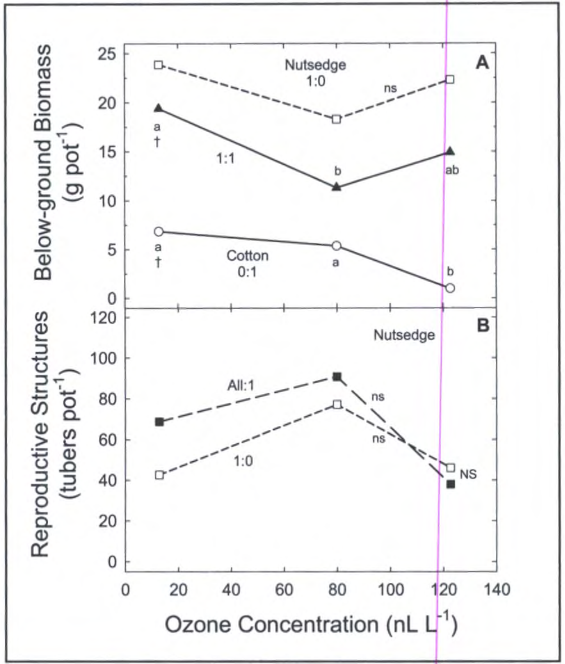

Figure 4. Effect of ozone exposure of the shoot on (A) below-ground biomass productivity of cotton (circles) and nutsedge (squares) grown alone and on the combined biomass of one plant of each species grown in direct competition (solid triangles) and (B) on the reproductive effort of nutsedge grown alone (1:0; open squares) or averaged over all population ratios (All:1; solid squares), expressed as number of reproductive structures per plant (B). Mean separation as in Figure 1.

Below-ground biomass of nutsedge grown alone was not affected by O_3 (Fig. 6; squares). However, the below:above-ground biomass ratio , a more sensitive parameter, was significantly affected by ozone, with a decline at medium and increase at high ozone concentration, reproducing the pattern observed, above, in the cotton system.

The number of tubers produced by the nutsedge plants increased with the number of seedlings initially planted in each pot (Fig. 7). However, the presence of a tomato plant reduced the number of tubers relative to nutsedge grown alone at all ozone concentrations (Fig. 7), as observed in previous studies (Morales-Payan; 2003).

When grown alone, aboveground productivity of tomato was more sensitive to moderate O_3 concentration than was that of nutsedge (Fig. 5A). However, at HO3 the relative sensitivities of the two species were quite similar. In these studies, tomato exhibited a distinct competitive advantage over nutsedge in light interception, confirming earlier results (Santos et al., 1997). Exposure to O_3 further established this aerial dominance, as nutsedge shoots were more erect in the LO3 and MO3 treatments than at HO3. At the highest O_3 exposure nutsedge shoots appeared less rigid, and exhibited a more prostrate growth habit, and even visibly healthy leaves were often observed hanging over the edge of the pots.

Below-ground productivity was also more sensitive in tomato compared to nutsedge (Fig. 6) as below-ground biomass of tomato declined with increasing O_3, whereas nutsedge increased slightly due to stimulated allocation to reproductive tubers. Overall, nutsedge was more tolerant to moderate O_3 concentrations than was tomato, with a substantial shoot response and enhanced allocation to tubers observed only at high ozone, whereas tomato responded progressively to increasing ozone concentration (Fig. 5,6).

Thus, in cotton any increment of ozone concentration, above that of charcoal filtered air, weakened cotton more than it did nutsedge and shifted the competitive advantage to the weed. In tomato, in contrast, this was true only at medium ozone and was reversed at high ozone, where nutsedge was the more sensitive species.

In the tomato system, exposure to high ozone stimulated biomass partitioning into reproductive structures (tubers), relative to the medium regime. Enhanced allocation to reproduction is a commonly observed plant stress response.

Tuber production in our studies has consistently appeared to be stimulated by O_3, though generally not significantly. As enhanced tuber production would lead to greater distribution and persistence of this weedy species in cultivated and other systems, this is a serious concern.

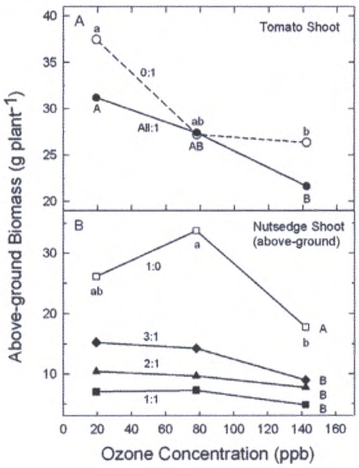

Figure 5. Effect of ozone exposure on development of above-ground biomass of (A) tomato (shoot) and (B) nutsedge (shoot minus rhizomes and tubers). Open circles represent each species grown alone. Closed symbols represent the levels of competition specified as population ratio of nutsedge:tomato.

The situation was similar for the critical root to shoot biomass ratio (R:S). This parameter and its associated leaf area-specific root hydraulic conductance (Grantz and Yang, 1996), are critical indicators of plant response to ozone.

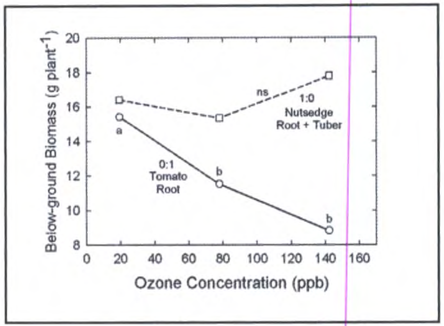

Figure 6. Effect of ozone exposure on development of below-ground biomass of tomato (circles; roots) and nutsedge (squares; roots plus rhizomes and tubers) grown alone.

Conclusion

Rising tropospheric ozone concentrations in rural, agricultural, areas has the potential to cause substantial changes in the management of weedy species in croplands. Similar changes may occur in vegetation management programs along highway and canal banks, and other non-agricultural settings. The specifics of ozone impacts on competition appear to be crop species specific. Further mechanistic details regarding competition above and below ground will be required to allow prediction of such competitive outcomes in future atmospheres. The frequently cited direct effects of ozone on crop yield loss represent only one important aspect of the general impact of changing ozone exposure patterns on crop production.

Acknowledgements

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Agricultural Pesticides as Sources of VOC Precursors of Photochemical Ozone

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Abstract

This project investigates the photochemical tropospheric ozone (tO3) formation potential of Volatile Organic Compounds (VOCs) from agricultural pesticide applications. One class of pesticides, emulsifiable compounds, is often formulated with highly volatile solvents as carriers. These solvents, in addition to the pesticidal chemicals themselves, are VOCs potentially contributing to ozone formation. A common formulation of chlorpyrifos accounts for a substantial portion of the highly reactive solvents used in the San Joaquin Valley (SJV) of California, where compliance with tO3 concentration limits remains a persistent challenge. This project investigates the volatility characteristics of each component of the selected chlorpyrifos formulation under ideal conditions to establish the relative volatility of the carrier solvent and longer half-life of the chlorpyrifos. Time courses of emission rates of both chlorpyrifos and the carrier solvent are then measured following field application of the pesticide formulation. The resulting data are used to speculate on the effectiveness of shifting the timing of pesticide application away from peak tO3 hours for mitigating tO3 concentrations in the SJV.

Rationale

Almost all past research on pesticides in air has been done on the "active ingredients", or AI. In contrast, the AI portion of chlorpyrifos pesticide formulations PF is presently low priority for two reasons: (a) it is known from past studies, that the AI is of sufficiently low volatility, such that its maximum incremental reactivity (MIR) cannot or will not be determined*; (b) without supporting information such as MIR, any data generated on the AI would be of no use for ozone formation estimations. Even though chlorpyrifos is referred to as a 'semi-volatile' in terms of laboratory analysis, this is relevant for a gas chromatograph operating at temperatures above 200C, which is very greatly in excess of ambient temperature maximums (including all-time records in California or elsewhere) of about 50C. Therefore, the main chemicals in our present study are the solvents used in the chorpyrifos PF, of which a major group are xylenes that have well-established MIRs.

Because ALL past research appears to have been performed on the semi-volatile AI and NONE on the rest of the PF (e.g. xylenes), we have determined that: (a) past research on chlorpyrifos, whether using the AI alone or as the PF, have no data on non-AI volatiles and therefore no information regarding the xylenes; (b) almost none of the past methods are useful for determining the emission of VOC (e.g. xylenes) from crop applications.

The disconnect in methods arises because the chlorpyrifos is designed for retention in the crop zone or canopy, while VOC such as xylenes are selected for providing solubility and for dissipation, in part to minimize harm to plants. The vastly different physico-chemical properties between AI and VOC means that different methods must be used for xylenes.

It is probable that air sampling methods for AI can't be used for xylenes, so we must evaluate such basic steps in the research. AI-based methods such as Teflon sheets for application rate/loss/overspray will almost certainly produce erroneous information for xylenes.

An extensive literature search has turned up NO methods for xylenes in PF applications. The first phase of our research is to develop a viable air sampling method that meets our analytical needs. This is currently underway. Only when we have a viable analytical method, can we turn to an initial field trial, which is in the planning stages now.

Method Approach

Ideally, a circular plot will be defined within which natural variation of terrain, plant stand, soil characteristics, etc. is limited. The plot will be large enough to be sprayed using conventional (industry typical) application equipment and small enough for application to be completed within a couple of hours at most. A tripod with a tall (30 foot) mast will be erected in the center of the plot so that the width of the pesticide-applied swath is equal in all directions. Since the sampling height must greatly exceed the plant canopy, cotton or alfalfa are preferred over orchard crops. Under this scenario, wind from any direction will provide the samplers on the mast equal concentrations of VOC assuming homogeneous volatilization from all points in the plot. Sampling will begin immediately upon completion of PF application plus anchoring of the second pair of guy-wires and will only be interrupted for changing the sampling cartridges. Personnel will wear appropriate protective clothing and ventilation for the required initial period – 24hours, perhaps.

A similar plot near the experimental plot but far enough away to avoid being impacted by the spray activity (a couple of miles) will be identified for background sampling. A single sample will also be collected 50 meters downwind of the downwind edge of the plot during application (beginning at the start of application and ending when application is complete for a time integrated sample of the entire operation). If wind speed and direction are adequate for dispersion modeling, concentrations measured upwind and downwind of the plot during application will be used to estimate emission rates during application. If wind speed is below 0.5 meters per second, the downwind sample may still provide an estimate of the relative importance of drift.

Site parameters

A circular plot such as that described above is agronomically atypical. Ideally, a square field can be found isolated from fields where the PF of interest is going to be applied during the experiment and where the corners of the field can miss an application without creating great hardship for the farmer. The site must also be isolated from significant structures or tree canopies that would create a wind shadow (no buildings or orchards within a half mile). The mast will be constructed in the center of the field and erected, creating a footprint of about 10 ft^2. As soon as application is complete, sampling will begin. Sampling can then continue until measured concentrations reach background and/or until neighboring fields require an application of either chlorpyrifos or other product containing the VOC -- which eliminates the required ambient background.

Experimental parameters

Sampling medium which has been bench-tested to be quantitative for all of the compounds of interest (AI and VOC) will be deployed at 5 heights from 0.5 to 9 meters above ground on the mast. A low (0.1-2.0 L/min) flow rate through the media will be maintained using battery operated pumps. The flow rate will be measured using an mass flow meter at the start and end of each sampling period for use in calculating total air volume. The pumps will be powered with rechargeable batteries which will be changed as needed and/or supplemented with solar panels. Upwind sampling will be accomplished with similar hardware but, assuming much lower concentrations to be present, several sampling periods on the mast may be integrated by time to one period at the background location (e.g. the background may run one time integrated sample for the first 24 hours while the samples on the mast are changed every 4-6 hours).

Model Calculation Results

Finally, our initial results from model calculations suggest that evening application of xylene based pesticides may result in 50% reduction of VOC (by chemical reaction during the night) before sun-light can commence photo-chemical production of ozone in the morning. However, under common rural conditions, there is still ample VOC for the same level of ozone to be reached in the course of the day.

* Personal communication from M. Benjamin, CARB.

Predicting Dust Concentrations Downwind from Eroding Sites

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Abstract

Soil erosion is a process of detaching and moving soil particles. The process is driven by energy transfer to the soil surface from flowing air or water and as well as particles such as raindrops or saltating soil grains impacting the surface. Suspension occurs when vertical fluctuations of the fluid exceed the settling velocity of the detached particles. Depending on the settling velocity and hence particle size, concentrations decrease vertically moving away from the source at the surface.

During the wind erosion process, the movement of soil along the surface rapidly increases with length of the eroding site because saltating particles enhance the return of detachment energy to the surface. This erosion process produces a line source potential for dust suspension that varies with length along the eroding site. Above the line source, a dust plume develops which increases in height as a function of site length. Dust concentration depends on both the mass of dust in suspension and the volume of air in the plume through which the dust is suspended. Dust concentrations, thus, vary both vertically and horizontally above the eroding site.

When the dust plume leaves the eroding site, it continues to grow until it reaches a height limit in the atmosphere, such as a temperature inversion or edge of front. Suspended particles settle out from the plume and are not renewed by the erosion process downwind from the erosion site. Thus, dust concentrations continue to change after leaving the eroding site and rapidly decrease because of the growth in plume height. When the plume reaches it maximum height, dust concentrations slowly decrease as an exponential decay function of length of travel. An overview of the concepts used to develop mathematical functions that describe this process and the changes in dust concentration as a function of height and distance downwind from dust sources is presented.

Background and Introduction

The accurate prediction of dust concentration downwind from eroding sites depends primarily on an accurate description and prediction of the detachment or erosion process. While many models exist that predict soil erosion by wind, one of the most accurate methodologies has been developed at Texas Tech University. This method is known as TEAM (Texas Tech Erosion Analysis Model) (Gregory et al., 2004). TEAM predicts the rate of soil movement as a function of the length of the eroding area, soil type and conditions, soil cover, wind speed, and relative humidity. Currently, it is assumed that the rate of soil movement is that predicted by the TEAM model. TEAM has successfully been used for both agricultural and industrial settings and defaults to a maximum transport equation when soil conditions approach that of sands found in desert regions. It is, thus, a very robust model in terms of variations in soil conditions over which it can be applied.

Dust concentration at ground level at any point along an eroding site can be calculated by dividing the predicted rate of soil movement per unit width by the volume of air containing the soil mass. The volume of air containing the soil mass is defined as the depth of wind containing the mass times a unit width times the average wind velocity in the horizontal direction in this cross section. Most movement associated with the wind erosion process is in the mode of saltation: a process of detachment then a return of the detached particle to the land surface where new detachment occurs from the kinetic energy of the incoming particle and the wind driving the particle. On the average, particles moving in saltation move only a few centimeters above the surface. A few particles may reach a height of 0.5 meters above the surface, but the main mass is very near the surface. This process is easily observed in snow or sand movement across roads. For this work, the average height of saltation is used as the height for estimating wind velocity in calculation of the air flow containing the detached soil. Twice the average height of saltation is used herein to define the depth of wind containing the material. Experiments in a wind tunnel (Wilson, 1994; Singh,

1994) indicate the distribution of soil particles to be very non-linear in this zone. Nevertheless, the present definition of dust concentration is a reasonable approximation of the average dust concentration just above ground level.

Suspension is a totally different process from detachment and movement by saltation. Unless particles are rotational, they have balanced forces acting above and below. There is a drag force that moves the particle downwind but no net upward force to lift the particle higher. Suspension occurs when the local air mass or eddy containing the particle moves up and carries the particle or particles with it. For this to occur, the particle must have a settling velocity less than the upward velocity of the eddy. Hence, small diameter and low density particles (aggregate particles compared to solid particles) move up and large diameter particles tend not to move into suspension. Based on conservation of air mass, the volume of air that moves up must be offset by an equal volume of air that moves down. Even though there is no net movement of air mass, there can be a net upward movement of suspended particles because the air near the surface has a higher concentration of particles than the air higher in the atmosphere associated with the downward movement of air masses. Even if the air masses above and below start with the same dust concentration, the system would redistribute the dust concentration to produce high concentrations near the surface and lower concentrations away from the surface. In the upward movement step, the rate of movement is the eddy velocity minus the settling velocity. In the downward step, the rate of movement is the eddy velocity plus the settling velocity. Thus, particles will move downward more readily than up. At steady state conditions, the rate of downward movement of dust equals the rate of upward movement. Equations to describe this process will be presented in a more detailed paper to follow and will be used to generate dust concentration variations with height and particle size. The objective of this paper is to present an overview of the system in which these suspension equations operate.

Dust Plume Limit

The height of the dust plume is one major limit or boundary condition affecting to the suspension of dust particles. This limit is visually detectable above eroding areas and downwind from eroding sites. Plume height is near zero at the beginning of the field or more technically at the beginning of the surface roughness conditions associated with the eroding site. It then increases in height with length downwind. Dust concentration (recognized as darkness or opaqueness in the plume) increases at ground level as the length of the eroding site increases. This observation matches the increase in predicted soil movement with length from the TEAM model. The top of the dust plume is often irregular revealing up eddies or gust of wind moving sediment upward. Nevertheless, there is a general shape of dust plume associated with length along the eroding site. This observable height of plume is the upper limit to the suspension process. Thus, to accurately predict dust concentrations above and downwind from eroding sites, this upper boundary must be included as part of the system.

This upper boundary or dust-plume boundary is best viewed as a boundary within a boundary. Surface winds that drive the wind erosion process are produced as a boundary condition from air movement over the land surface. Thus, the whole wind system is a boundary layer that produces an average wind velocity with height that follows a logarithmic or power equation distribution as a function of height. Horizontal winds increase at a decreasing rate with distance above the land surface. Equations that govern this process can be found in most fluid textbooks that deal with open channel flow or flow in the atmosphere. When a new surface condition is encountered by the wind, it starts to shape the wind velocity profile producing a different set of characteristics from the previous surface condition. The difference between the old and new conditions is detectable, increasing in height as a function of fetch length, length downwind from the beginning of the new surface conditions. The literature defines this change in wind profile conditions as an internal boundary layer (Elliott, 1958). Elliott (1958) has shown this internal boundary layer not to be a function of wind velocity but is a function of surface roughness conditions.

It appears that the same process creating the internal boundary layer is also involved in creating the dust plume above eroding sites. If true, then knowledge and equations developed to predict the internal boundary layer can also be used to describe the upper limit for the suspension process. Elliott (1958) provides a relatively simple empirical equation to predict the height of the internal boundary layer. Elliott's equation, however, is too simple to match the boundary conditions for the upper conditions in the atmosphere or for long distances downwind from the eroding site. An alternative equation to Elliott's equation is used in the current dust concentration models. The alternate matches the required upper boundary conditions and produces results that closely match Elliott's equation near the surface. The equation used to predict the height of the internal boundary layer and, thus, the height of the dust plume above and downwind from eroding sites is a saturating exponential function with independent variables of fetch length and height of the boundary layer in the atmosphere. The typical heights for the boundary layer during wind erosion events are about two thousand meters for frontal events and four to five thousand meters for events produced by down mixing of winds from aloft.

There is some question about what to do when the dust plume leaves the eroding site. In theory, a new surface condition is encountered and a new internal boundary layer begins. The new internal boundary layer should produce a clean air boundary below the dust plume similar to clean air below a plume downwind from a smokestack. We, however, do not see this condition downwind from eroding sites. Instead, we see dust. In fact, there have been major car accidents downwind from eroding sites because of the reduced visibility near ground level downwind from eroding sites.

It appears that the new internal boundary layer that should form due to the new surface condition is masked by sediment and heaver sediment-laden air settling and mixing into the lower less dense layer. Thus, we continue to grow the old internal boundary layer as the upper limit for the dust plume and the upper limit for the suspension process.

It should be noted that predicted dust concentrations and observed visibilities rapidly change with distance downwind from eroding sites because the same amount of sediment is now distributed in an increasing volume of air as the dust plume grows in height. This rapid decrease in dust concentration and increase in visibility continues until the dust plume reaches the height of the boundary layer producing the wind. After the dust plume depth reaches the height of the boundary layer, dust concentration decrease at a much slower rate as a function of loss of sediment and widening of the plume.

Loss of Sediment

As the dust plume moves downwind from the erosion site, sediment particles may drop out and not become re-detached. The rate of this sediment mass loss is a function of dust concentration in the zone immediately above the land surface and the settling velocity of the sediment. Sediments with large particle sizes settle out more rapidly than sediments with small diameters. Once the dust plume height has reached its maximum height, the loss of sediment and loss in dust concentration becomes an exponential decay function of distance traveled by the plume. This relationship is verified by observations that monitored dust concentrations which began in China and traveled across the Pacific (Arimoto, 1989).

There are other processes that can remove sediment from a dust plume. Rain, hail, or snow all can trap sediment particles and quickly move them to ground level. Dust laden rain, hail, and snow have all been observed in West Texas, sometimes on the same day. These methods of sediment removal are not considered in the current model, however, they are part of nature's way to filter air and improve air quality.

Summary of Modeling Process

In the current model, the concentration at ground level is estimated from the erosion process with TEAM. Next, the upper boundary for dust concentrations is estimated with an equation for internal boundary. The third step is to remove sediment from the lower boundary of the dust plume by settling particles across the lower boundary. The total sediment at a specified distance downwind is then redistributed from ground level to the maximum height of the plume. The redistribution is performed for each particle size of interest. Generally, the particle size distribution of the soil is used to establish five to seven size classes of particle. The masses from each of these particle size redistributions are summed to get total mass of sediment at heights of interest. The total sediment concentration at a given height is then determined by dividing the mass of sediment by the volume of air containing the sediment. The process is feasible but tedious—a good use of computer technology.

The current model uses representative particle sizes with deterministic equations to describe a system of continuous particle size distributions and random or stochastic variations in vertical wind speeds to make calculations. The solution is only approximate. However, it is built on known relationships in the literature and relationships that can be derived from physical principles. This leads to a relatively robust process-based model that describes the soil erosion and dust generation processes caused by wind.

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Release and Measures to Reduce Generation of Dust in Fattening Pig Houses

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Abstract

The mass balance of dust as well as the efficiency of different dust reducing measures in fattening pig houses have been investigated and analysed.

Investigations showed that the generation of dust is influenced by the number and the weight of the pigs. Settling of dust is a more important mechanism in the mass balance of dust than ventilation rate. A major part of the generated dust settles on different surfaces inside the buildings. The settling rate of dust is affected by the concentration of dust in the air. The settled amount of dust also stands in relation to the floor area of a stable.

An increased ventilation rate has a limited effect on the concentration of total dust due to the importance of the settling of the dust. However, it has been observed that the type of ventilation technique may influence concentration of respirable particles. Also the type of housing system influence the generation of dust. One factor which has a strong influence on the concentration of dust is the activity in the buildings.

Dust reducing measures as electrostatic air cleaning of the air and removal of dust with vacuum cleaners had limited influence on dust concentration.

Automatic spraying of small droplets of water reduced the dust concentration with two types of spraying nozzles. For another type of nozzle the generation of dust increased due to an ultra sound which created an increased activity of the pigs. Spraying with a mixture of rape seed oil was also effective with manual spraying as well as with an automatic spraying system. The oil seemed to have an effect on the generation of dust from the skin but also to function as a dust binding agent for settled dust.

Introduction

The presence of dust in pig houses may create working environmental problems (Donham, 1987; Tielen et al., 1995; Takai and Iversen, 1990; Larson et al., 1993; Malmberg et al., 1993) as well as depressed health status of the animals (Donham, 1991; Robertson et al., 1990; Robertson, 1993; Hamilton et al., 1993). Measures to reduce the contamination of the air in swine confinement houses are therefore urgent. The purpose of these investigations has therefore been to analyse the mass balance of dust but also the effectiveness of different dust reducing measures.

The major part of swine house dust is organic. Originally, the dust was considered to origin from feedstuffs. However, investigations (Hartung, 1992) have indicated that there are also other components of the dust as particles from skin, hair and faeces. Investigations (Angst, 1984; Hartung., 1992) have shown that the composition of settled dust and feedstuffs in pig houses differ considerably regarding crude protein and crude ashes.

The major part of the number of dust particles are respirable (Nilsson, 1982). However, it should be observed that the major part of the weight of the dust is not respirable. Donham (1986) reported that 7 % of the total weight of the dust was respirable.

A considerable proportion of the dust seems to originate from the pigs themselves. Nilsson (1982) found that the type of feed (dry or wet) had limited influence on the daily averages of total dust concentrations in growing-finishing pig houses. However, both in cases with wet and dry feed the dust concentrations increased during the feeding time due to an increased activity.

Several investigations (Nilsson, 1982; Gustafsson, 1994; Pedersen, 1993; van't Klooster et al., 1993) have proved that the activity in swine houses has a strong influence on the concentration of dust in the air. The concentration normally increases during periods when the activity is high, such as during feeding, weighing of the pigs, etc. The influence of feeding technique on the activity of the pigs may have an indirect effect on the dust concentration (Robertson, 1992). Pedersen (1993) has shown that the number of dust particles in the air varies with the same pattern as the signal from an activity sensor.

There is little consensus among investigations about the influence of ventilation on dust concentration. However investigations (Bundy and Hazen, 1975; Bundy, 1984) about the influence of ventilation rate on the number of dust particles have shown a decrease in number of dust particles at increasing air flow rate. The influence of ventilation rate on total mass concentration of dust in the air has been less pronounced (Nilsson, 1982; Gustafsson,1994). Investigations have also indicated influence of different ventilation techniques on dust concentrations (van't Klooster et al., 1993).

Theory

The mass balance of generated dust can be described as:

$$V\frac{dC_{av}}{dt} = p - q(C_o - C_i) - SA - G \qquad (1)$$

where: V is the building volume in m^3 ; C_{av} is the average dust concentration; C_o and C_i are the total dust concentrations in outlets and inlets in mg/m^3 ; t is time in h; p is the production of dust in mg/h; q is the ventilation rate in m^3/h; S is the settling rate of dust in mg/ m^2 h; A is the area of the floor in m^2; and G is the amount of dust removed by air cleaning devices in mg/h.

The settling of dust may be described by:

$$S = v\ C_{av} \qquad (2)$$

where v is a value depending on the properties of the dust in m/h.

If stationary conditions are maintained, is it possible to determine the generation of dust from:

$$p = q\ (C_o - C_i) + S\,A + G \qquad (3)$$

The fraction removed by air cleaning devices is described by:

$$G = \theta\ q\ \eta\ C_{av} \qquad (4)$$

where θ is the relation between the air flow rate of an air cleaner and the ventilation rate of a barn and η is the air cleaning efficiency of an air cleaning device. The concentration in the inlet of the air cleaner is assumed to be the average dust concentration in the air C_{av}.

Material and Methods

Buildings and Equipment

The investigations were carried out in three piggeries for growing-finishing pigs at the research station Alnarp Södergård.

The influences of the following factors in the building environment were investigated, namely: number and weight of pigs; activity; settling of dust; ventilation rate; ventilation technique; and animal housing system.

The following methods to reduce the generation and concentration of dust were also investigated, namely: electrostatic air cleaning; dust removal by vacuum cleaning; humidification of the air with different spraying nozzles; and oil treatment.

Measurements

The efficiencies of different treatments were analysed by: gravimetically measurements of the amount of total dust in mg/m^3 with 37 mm diameter dust filters (Millipore) located in the middle of the barn at 1.5 m height but also in the exhaust air; gravimetically measurements of the amount of respirable dust (mg/m^3) with dust filters (Millipore) after separation of particles larger than 5 µm with a cyclon (SKC cyclon) at the same locations as for total dust; counting the number of particles of different sizes with an optical particle counter (Rion) which counted the number of particles of sizes larger than 0.3, 0.5, 1.0, 2.0 and 5.0 μm; weighing settled dust on five 0.230 m^2 settling plates located at a height of 2.0 m with the collected amount of dust measured by weighing the plates on a balance; measuring the ventilation rate with a hot wire anemometer (Alnor) in exhaust air ducts.

Each measurement was carried out over a period of 3-4 days in order to collect enough dust on the settling plates. Different treatments were compared to reference values measured before and after the treatments.

Analyses

Different measures to reduce the generation and concentration of dust were analysed by using the following properties in the mass balance Eqn (1): averages of total and respirable dust concentrations C_{av} measured in the middle of the barn and in the exhaust air; average of settling rate of dust on settling plates S; generation of dust p as defined by Eqn (3); relation between settled amount of dust and dust concentration S/C_{tot}; and fraction of respirable dust C_{resp}/C_{tot}.

Measurements of the number of particles were mainly used to get a picture of the particle size distribution and influence of activity and ventilation rate.

Results and Discussion

The influence of number of pigs on production of dust was investigated by changing the number of pigs when their average body weight was in the range of 86 – 98 kg. The measurements showed that the generation of dust is proportional to the number of animals (Figure 1).

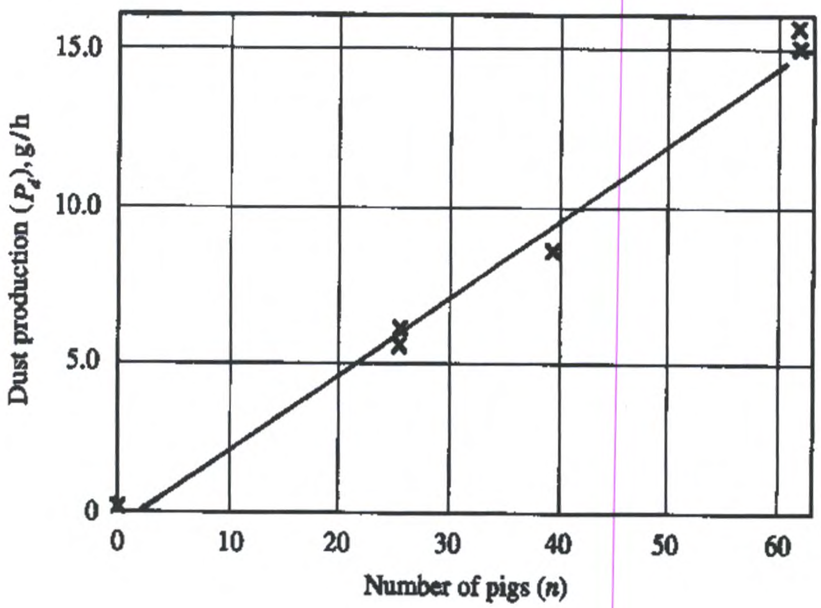

Figure 1. Relation determined between the production of dust and the number of pigs.

The influence of pig weight on dust production was also investigated during 14 production batches with growing finishing pigs. The production of dust increased with the body weight in all batches.

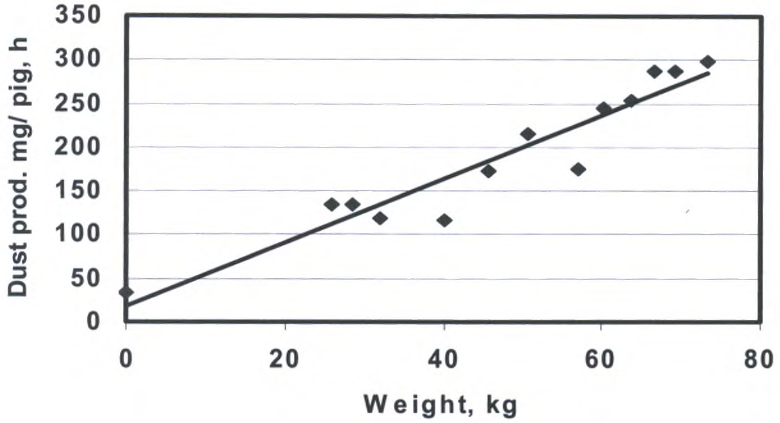

Figure 2. Relation between dust production and weight of pigs

The settling rate of dust varied to a large extent between different locations inside the buildings. However, it was also found that the variations in the settling rate followed the same pattern over the entire production periods. This fact indicates that the air flow patterns inside the buildings could have an influence on the dust conditions.

An example of relation between settling rate S and the total dust concentration C_{tot} is presented in Figure 3. Determinations indicate that the settling rate of the dust is influenced by the concentration of dust in the air.

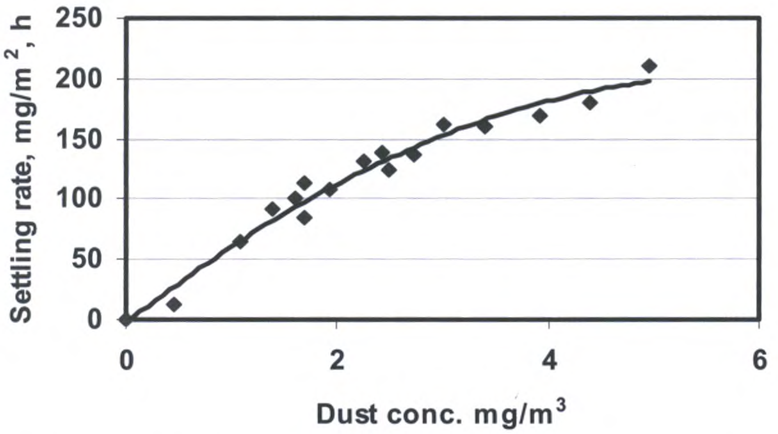

Figure 3. Relations determined by linear regression between the settling rate and the concentration of total dust during a production batch with growing- finishing pigs.

Increased ventilation rate is often recommended as a method to reduce the concentration of air pollutions in buildings. Unfortunately, the ventilation rate has a limited diluting effect on dust at those ventilation rates recommended for insulated pig houses in temperate areas. The reason is that the settling of dust on different surfaces is a more important mechanism to remove dust particles from the air than the ventilation rate in pig houses. The major part of the dust settles on different surfaces inside the buildings. Figure 4 shows an example of the limited effect on total dust concentration at different ventilation rates. The dilution of the dust by increased ventilation will increase the heating requirement in temperate regions.

The fraction of the generated dust which is exhausted by the ventilation air is presented in Figure 5. The fraction of the dust which is exhausted is limited at those ventilation rates which occur in swine confinement houses in temperate areas. The low fraction of exhausted dust shows that the settling of dust is more important than ventilation rate in the mass balance of dust.

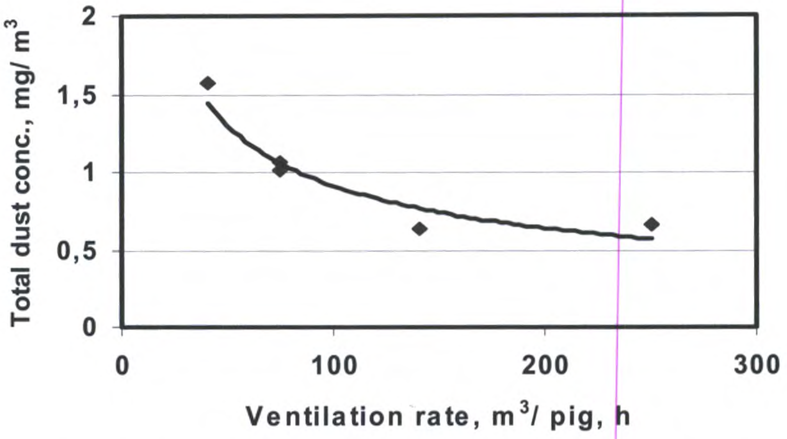

Figure 4. Example of influence of ventilation rate on total dust concentration.

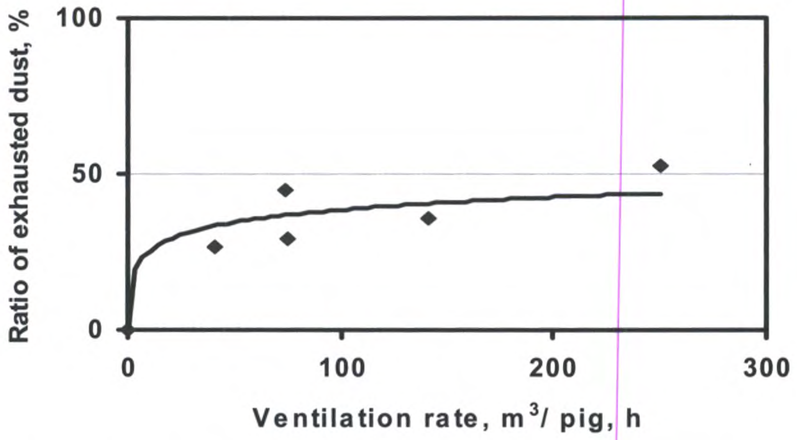

Figure 5. Ratio of dust extracted by the ventilation system to dust production.

The influence of ventilation rate on the number of dust particles of different sizes when air was supplied with a high speed recirculating air inlet is presented in Figure 6. The ventilation had a diluting effect mainly on particles larger than 1.0 μm. The ventilation rate had no effect for particles smaller than 1.0 μm for this particular ventilation system.

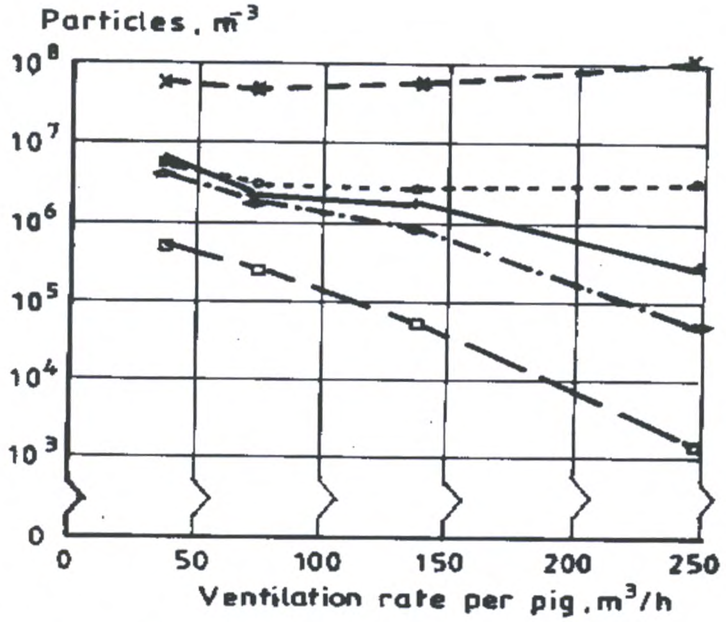

Figure 6. Influence of ventilation rate on the number of dust particles of different sizes; x ___ ___ x, 0.3-0.5 μm; o _ _ _ _ o, 0.5 -1.0 μm; +_______+, 1.0- 2.0 μm; ♦ __ . __ ♦, 2.0- 5.0 μm; ____ ____, > 5.0 μm

Two very different ventilation principles were compared, namely: high speed recirculating air inlets in combination with an exhaust fan located at roof level (high exhaustion); and a porous ceiling as the air inlet in combination with manure gas ventilation (low exhaustion).

The recirculating air inlets create considerable air mixing and air movements in the stable while the air movements from the porous ceiling are extremely small.

Experimental data for dust concentration and production, settling rate, ratio of respirable dust and fraction of exhausted dust are presented in Table 1. Significant differences ocurred regarding respirable dust concentration C_{resp} and S/C_{resp}. These results indicate that the ventilation technique (mainly air velocities and air movements) may have an influence on small particles.

Table 1. Total and respirable dust concentration C_{tot} and C_{resp}, dust production, ratio between settling rate S and total and respirable concentrations, ratio of respirable to total dust concentration and fraction of exhausted dust at two different ventilation techniques.

	High speed air inlet + high exhaustion			Breathing ceiling +low exhaustion			Difference,	
Parameter	x	s.d.	n	x	s.d.	n	%	
Total dust conc., mg/m^3	1.29	0.57	10	1.14	0.32	7	+13	NS
Resp. dust conc., mg/m^3	0.26	0.095	6	0.15	0.061	4	+77	*
Dust prod. per pig, mg/h	253	104	11	322	116	6	-21	NS
S/C_{tot}, m/h	86	41	11	69	12	7	+24	NS
S/C_{resp}, m/h	392	86	6	535	80	4	-27	*
Ratio of resp. dust, %	18.8	3.5	6	14.2	4.8	4	+32	NS
Exhausted dust, %	25.9	7.3	9	21.0	6.0	5	+23	NS

x, average; s.d., standard deviation; n, number of batches; N.S., non-significant difference;
*, significant difference 0.05 >p >0.01

Two different housing systems were compared namely: climate controlled confinement in an insulated piggery; and cold confinement in an uninsulated piggery with straw bedding and natural ventilation.

In all investigated batches except one, significant differences occurred between the different piggeries, see Table 2. The presence of dust was much lower in the uninsulated stable with straw bedding. The reasons to the large differences between the different systems are difficult to explain. Possible explanations may be more moisture in the cold environment with straw bedding, and very high ventilation rates during spring, summer and autumn in the uninsulated stable.

Table 2. Total and respirable dust concentration C_{tot} and C_{resp} and settling rate of dust S at five comparative production batches with growing-finishing pigs in two different housing systems.

		Insulated and climate controlled			Cold confinement with straw bedding and natural ventilation			
Property	Trial	x	s.d.	n	x	s.d	n	Δ
Total dust conc.	1	1.26	0.57	10	0.19	0.06	15	-75 ***
mg/m^3	2	1.91	0.82	17	0.91	0.22	11	-52 ***
	3	1.00	0.40	14	0.39	0.1	14	-61 ***
	4	0.787	0.35	17	0.62	0.41	7	-21 NS
	5	1.37	0.59	23	0.45	0.15	23	-67 ***
Resp. dust conc.	2	0.30	0.23	5	0.096	0.087	10	-68*
mg/ m^3	3	0.09	0.05	11	0.034	0.036	13	-62 **
	4	0.14	0.07	16	0.215	0.146	6	+53 NS
	5	0.15	0.063	23	0.059	0.015	7	-61 ***
Settling of dust	1	67	22	21	30	20	20	-55 ***
mg/m^2, h	2	72	27	17	45	29	9	-38 *
	3	55	24	15	30	8	14	-45 ***
	4	63	25	17	63	25	20	0 NS
	5	71	22	23	52	21	22	-27 ***

x, average; NS, non-significant difference; s.d., standard deviation; n, number of batches; Δ, difference %; *, significant difference 0.05 >p >0.01; **, significant difference 0.01 >p >0.001; ***, significant difference 0.001 >p

The use of an electrostatic air cleaner had a limited effect on the dust concentration in the air, although it was proved that the equipment removed a large fraction of the particles in the air which passed through the device. Considering the mass balance of the dust, it is obvious that air cleaning devices need large airflow capacities if the dust concentration in the air should be affected. The airflow through an air cleaner has the same influence on the dust concentration as an equally large increase in ventilation rate in the building.

The use of a vacuum cleaner designed for industrial purposes, as well as a central vacuum cleaning system, were investigated. Both devices were used to clean floor surfaces but also other surfaces such as pipes, etc. at different cleaning intervals. Although most surfaces looked cleaner after the treatments, no significant effect could be measured regarding total and respirable dust concentrations, settling rate or generation of dust.

Three types of spraying nozzles were investigated in an automatic spraying system namely: high pressure (ultra sound) nozzles; flat fan nozzles; and full cone nozzles. The nozzles were operated automatically in short sequences. They were operated twice per hour from 8 a.m. until 6 p.m. and once per hour during the rest of the day.

Spraying water droplets have given different results depending on the type of nozzles which were used. The use of ultra sound nozzles which created droplets in the size range between 5 and 10 μm resulted in a significant increase of both total and respirable dust concentrations during nine comparative trials. The reason for the increased dust concentrations was probably the ultra sound (frequency 30 kHz) created by the nozzles. This sound was outwith the human hearing range. However, observations of the pigs clearly showed that the pigs reacted in an abnormal way the first times the nozzles were in operation. The increased dust concentrations may only be explained by an increased activity of the pigs due to the ultra sound.

The use of the flat fan nozzles operated with a pressure of 0.35 MPa gave a reduction in both total and respirable dust concentrations. In these trials, each pen was equipped with four (horizontal spraying direction) flat fan nozzles in combination with a full cone nozzle (orientated downwards).

The use of full cone nozzles operated at 0.3 MPa pressure also reduced both total and respirable dust concentrations. The settling rate and the generation of dust were also affected. The efficiency was improved with increasing amount of water, see Figure 7.

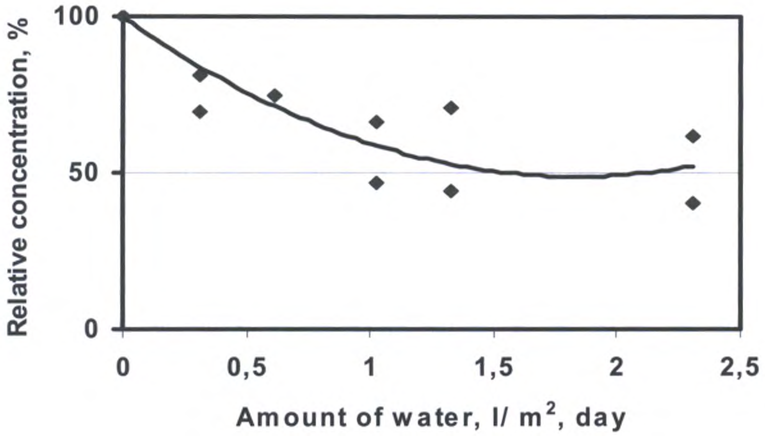

Figure 7. Relative change in dust concentration in % when different amounts of water were supplied with full cone nozzles.

It has earlier been proved by Takai et al. (1993) that the spraying of mixtures of oil and water in pig houses will give a significant reduction in dust concentrations. However, it has not been verified whether the reduction of dust is due to less generation of dust from the pigs skin surfaces or if the oil functions as a dust binding agent on different building surfaces.

In these investigations, 10% rape seed oil in a water solution was used. The mixture was applied in two different ways namely: manually spraying directly on the pigs with a knapsack sprayer; and automatically with a spraying system with full cone nozzles parallel to the feeding troughs. In the latter case, the oil mixture was applied once per day during the feeding time.

The manual treatment affected all the parameters measured. In order to see if the oil affected the release of dust from the skin, one treatment was carried out outside the building so that no oil should cover any building surfaces. In this treatment, the total dust concentration was reduced to 84% of the reference level. The treatment had a significant reduction on settling rate (63% of the reference level) and generation of dust (72% of the reference level). It can be concluded that the treatment with oil reduced the generation of dust from the skin to some extent but also that the oil treatment functions as a dust binding agent on surfaces in the building.

An automatic system for spraying of oil was also investigated. The automatic spraying system consisted of two full cone nozzles per pen located parallel to the feeding troughs. The oil mixture was sprayed over the pigs back once per day during the feeding of the pigs. The reduction on total dust concentration at different amounts of oil is presented in Figure 8. The treatments resulted in a considerable reduction in total dust concentration. Reduction levels in the range of 75-80% has earlier been reported by Takai et al. (1993) with a high pressure spraying system.

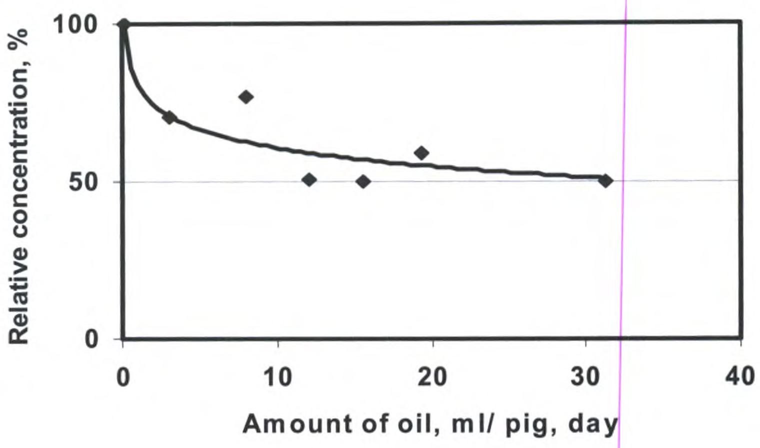

Figure 8. Relative change in total dust concentration in % when different amounts of oil were supplied with full cone nozzles.

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NH_3 Emission from Pig Husbandry in Relation to Ventilation Control and Indoor Air Cooling

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Abstract

Animal husbandry is known as one of the main contributors to agricultural NH_3 emission, which might lead to acidification and eutrophication of soils and waters. NH_3 is released indoors mainly from urine and stored excrements. Thereby, the NH_3 release is related to animal activity, pen fouling, ventilation, indoor temperature and humidity. The influence of ventilation and indoor air climate on the diurnal and seasonal emission rate of NH_3 was investigated in this research work. Different ventilation control strategies were tested in a research pig facility over a total of four fattening periods. Throughout this time, NH_3 concentrations were measured continuously by NDIR spectroscopy, indoors, as well as in the incoming and exhaust air. The ventilation rate was determined using calibrated measuring fans. The ventilation strategies featured adiabatic indoor air cooling, and either an increased, activity controlled, or reduced, CO_2 and temperature controlled ventilation rate. At days with mean daily outside temperatures above 14 °C, indoor air cooling resulted in a reduction of the diurnal maximum temperature by about 4 to 5 K, the ventilation rate was reduced by about 22 %. The combination of indoor air cooling and CO_2 control did furthermore reduce the ventilation rate by about 33 %, at mean daily outside temperatures above 14 °C, and by about 20 % for lower outside temperatures.

The mean NH_3 emission rate of the reference ventilation differed significantly between mean daily outside temperatures below and above 14 °C. Nevertheless, highest mean NH_3 emission rates, 130 g d^{-1} LU^{-1} and 120 g d^{-1} LU^{-1}, occurred during the two fattening periods in early and late spring. At mean daily outside temperatures below 14 °C, NH_3 emission were furthermore increased significantly for ventilation with evaporative indoor air cooling, in average by about 10 % to 14 %. In contrast, no significant differences in NH_3 emission occurred between the different ventilation strategies at warm outside temperatures above 14 °C. Hence, in order to reduce NH_3 emission by adiabatic indoor air cooling, an optimized fogging control, regarding complete evaporation of the water, was required. On a yearly basis (330 fattening days), the mean measured NH_3 emission rate ranged at 5,1 kg NH_3 pig place^{-1} year^{-1}.

Introduction

Main sources of NH_3 in animal husbandry systems are urine and excrements. Beside feed composition, mainly the storage duration and management of excrements in the stable, the indoor air climate, fouled surfaces, as well as the animals themselves exert an influence on the release of NH_3. Ventilation control directly influences the ventilation rate, the indoor temperature, and humidity, but also the fouling behaviour of the pigs, and thus the emission of NH_3. The influence of the indoor air climate on pen fouling and hence on the NH_3 emission rate was defined by Ni (1998) as floor factor and was calculated using the indoor temperature and the weight of the animals as input variables. The indoor temperature and air velocity exerts furthermore a dampened influence on the slurry temperature and thereby increases or lowers the release of NH_3 from the slurry storage (Berckmans et al. 1994). Nevertheless, high air velocities and turbulences might also increase the NH_3 release, caused by a dilution effect on the air above the slurry surface (Hartung, 1995). The quantification of the effects of different influencing variables which are contrary to each other and/or are related to each other, like the ventilation rate and the indoor temperature, can in general be difficult. Although the ventilation rate and NH_3 emission were clearly positive correlated (R^2 = 0.729) during investigations of Ni (1998) in mechanically ventilated pig facilities, no or even negative correlations between the ventilation rate and the NH_3 emission rate were found by Gallmann (2003) in a natural ventilated building for fattening pigs, in which the ventilation rate was not controlled by the indoor temperature. High variations in measured emission rates have their origins furthermore in different regions, facilities, ventilation systems, seasons, management, as well as in the varying emission course throughout the fattening period (Aarnink, 1997; Groot Koerkamp et al. 1998; Ni, 1998; Gallmann, 2003). The potential to lower NH_3 emission by ventilation control strategies can be estimated with up to 35 %, based on investigations on ventilation effects in mechanically and natural ventilated buildings (Keck, 1997; Ni, 1998; Gallmann et al., 2003). However, the verification of such a reduction potential in mechanically ventilated buildings during long term measurements is hardly performed. Thus, the aim of this investigation was to study the influence of evaporative indoor air cooling in a facility for fattening pigs on the emission of NH_3, and to compare the effects of different ventilation strategies, which use additional control variables (animal activity and CO_2 indoor concentration), and hence feature either an increased or a lowered ventilation rate.

Methods

Research Facility

Investigations on ventilation control, indoor air cooling, and NH_3 emissions were carried out in two separately compartments (54 pigs each, 0.9 m^2 pig^{-1}) at the research facility for fattening pigs (Hartung, 2001), University of Hohenheim. Fattening started at an average weight of 25 to 30 kg per pig. The measurements were performed until the pigs reached an average weight of approximately 105 kg. Each compartment featured two pens, equipped with a slotted concrete floor and a slurry pit underneath each pen (Figure 1). The pens were subdivided into a lying and feeding area and an excremental area, characterized by a ratio of the slotted floor area of 14 % and 6 %, respectively. Feeding was supplied either with a sensor liquid feeding system or an ad libitum mash feeder. The feed composition and protein content of the food was equal for both feeding systems and was adapted in fattening week 2, week 5, week 8, and week 11. Straw was supplied for occupation. The slurry was sampled in the slurry pits during fattening, and was completely remove after each fattening period (Haeussermann et al., 2004).

Ventilation System and Tested Ventilation Control Strategies

The mechanical ventilation system was designed as under-floor extraction, and was equipped with one separately controllable ventilation fan per compartment. Fresh air was supplied via two air inlet pore channels per compartment, each arranged centrally above the animal area. The ventilation rate was controlled either by temperature (Reference and Strat. B), temperature and animal activity (Strat. A), or by CO_2 indoor concentration and temperature (Strat. C) (Table 1).

Table 1: Overview on ventilation control strategies and control input variables

ventilation control strategy	**Reference - no humidifying -**	**Strat. B - humidifying -**	**Strat. A - humidifying -**	**Strat. C - humidifying -**
control variables*	Temperature^1	Temperature^{1,2} Humidity^2	Temperature^{1,2} Humidity^2 Animal activity^{1,2}	CO_2 indoor concentration^1 Temperature^{1,2} Humidity^2

* control input for: ^{1}ventilation rate ^{2}fogging system

For each of these ventilation strategies, the set temperature (T_{set}) decreased non-linearly from 25 °C to 16 °C during the fattening period. Using Strat. A, the ventilation rate was controlled by temperature but was increased during short-termed periods when the group animal activity was high. In contrary, the ventilation rate was kept on minimum at Strat. C until either the maximum value for the CO_2 indoor concentration (2000 ppm) or the maximum value for the indoor temperature ($\Delta T_{set} = 3$ K) was exceeded. The four ventilation strategies were distributed randomly on the two compartments and on the four fattening periods. At the first two fattening periods, each strategy was tested throughout three-week long measuring sections, once per compartment per fattening period. At the last two fattening periods, the ventilation strategies were tested twice per compartment per fattening period, but throughout half the length of a measuring section (10/11 days) at each time (Haeussermann et al., 2004).

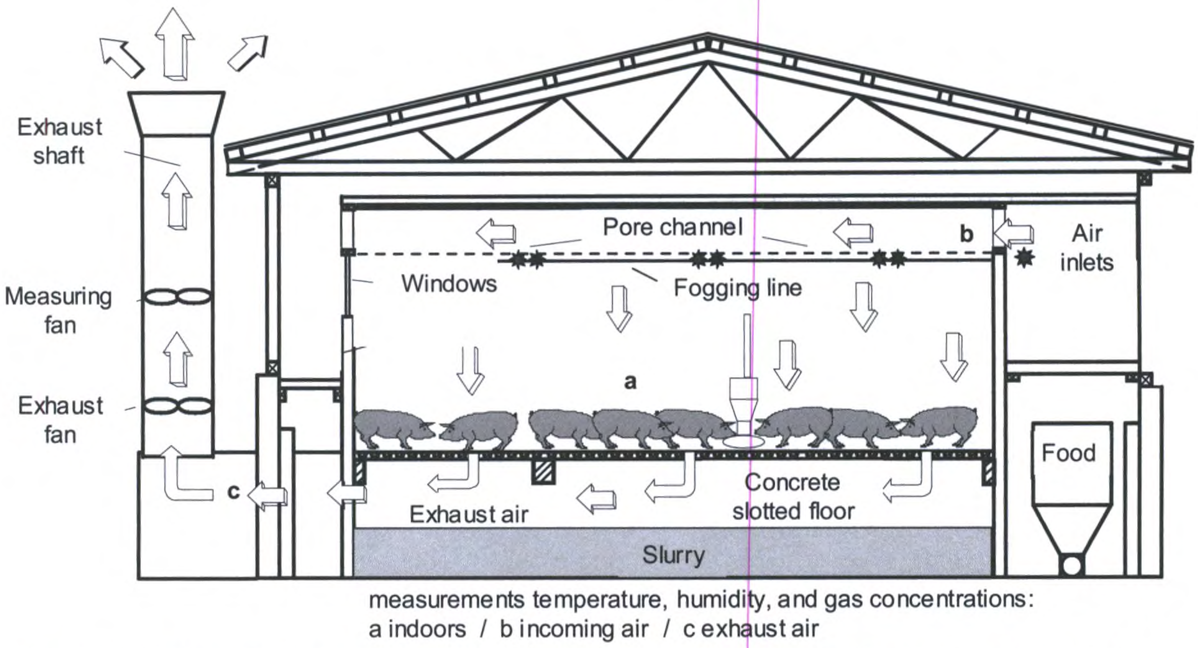

Figure 1. Vertical projection (west-east), research facility for fattening pigs, University of Hohenheim (modified, adopted from Hartung, 2001, Gallmann 2003)

Fogging System and Control

Two separately controllable fogging lines per compartment were used to cool down and to humidify the air (Figure 2). They were placed one inside the compartments (3 nozzles per pen) and a second one in front of the air inlets (2 nozzles per inlet). Water supply was 885 ml per minute per compartment when both fogging lines were operated. The pressure of the pump was fixed at 7 MPa. During the investigation, fogging was operated in a pulse-cycle, set on four minutes fogging-on and three minutes fogging-off. A fogging cycle started either when the indoor temperature rose to more than 1.5 K above T_{set} (Strat. B, Strat. C, and Strat. A), when the indoor humidity dropped below 50 % (Strat. B, Strat. C, and Strat. A), or by the signal of the group animal activity (Strat. A). Maximum indoor humidity was set on 80 % with a hysteresis of 10 %, minimum indoor temperature for fogging equalled T_{set}.

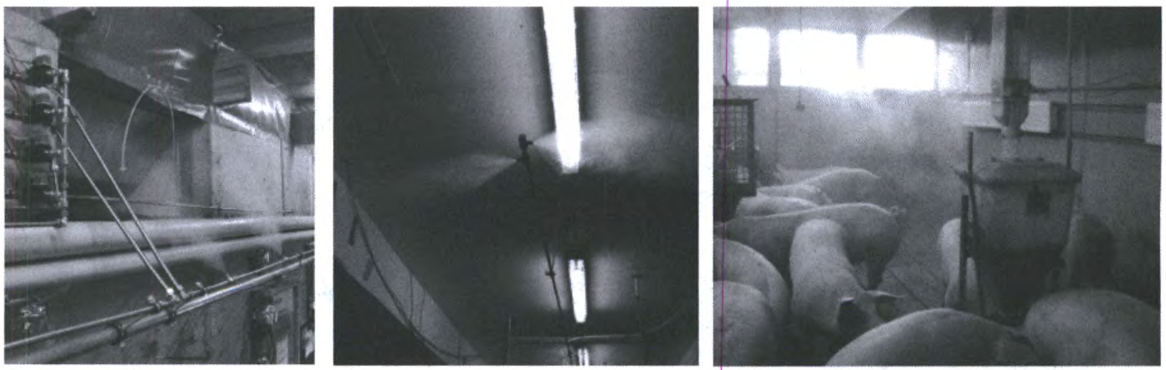

Figure 2. Air humidifying at the incoming air and indoors using separately controllable fogging lines with four and six high pressure nozzles respectively per compartment

Measurements

During a total of four fattening periods, outside and indoor temperature, relative humidity, and the group animal activity were measured continuously with one average value per 15 min (Table 2). NH_3 and CO_2 concentrations indoors, as well as in the incoming and in the exhaust air were measured at the same frequency using NDIR spectroscopic gas analyzers. For the gas analysis, the air was sucked through condensation protected Teflon tubes into the measuring chamber of the gas analyzers, placed in a temperate room outside the compartments. The air sampling was rotated every 150 sec between the six sampling positions (indoor air, incoming air, exhaust air of compartment 1 and compartment 2). An average value of the respective sampling position was calculated from the last 30 sec, while the first 120 sec were used to compensate maximum gas transport times as well as rise and decay times of the measuring instruments in relation to the high differences in gas concentrations between the sampling points. A correction of the measured NH_3 concentration was performed subsequently to the measurements according to the water vapour cross sensitivity of the gas analyser and the water content of the air at the respective sampling position (Brose, 2000). Parallel to the gas measurements, the ventilation rate was determined using a calibrated measuring fan (Table 2). The calculation of the NH_3 emission rate took into account the difference in the gas concentration at the exhaust and incoming air, the ventilation rate, as well as the animal weight, calculated as Livestock Units (1 LU = 500 kg). The strategies were compared by their mean values and inter-quartile ranges (25th and the 75th percentiles of the measured mean daily values).

Table 2. Measured variables, measuring instruments, frequencies and accuracies

	Measuring instrument	measuring range / accuracy	sampling rate	measuring frequency
Ventilation rate	measuring fan MULTIFAN	200 – 10000 m^3/h +/- 20 m^3/h	1 sec	15 min
Air temperature	resistance (PT 100) Hygroclip, ROTRONIC	- 40 to + 85 °C +/- 1 °C	1 sec	15 min
Relative humidity	capacitive Hygroclip, ROTRONIC	0 – 100 % +/- 1 %	1 sec	15 min
Animal activity	passive infrared sensors (Pedersen and Pedersen, 1995)	0 – 5 V (scale)	1 sec	15 min
CO_2	NDIR – Spectroscopy Unor 610, MAIHAK	0 – 10000 ppm +/- 10 ppm	1 sec	15 min
NH_3	NDIR – Spectroscopy Binos 4b, ROSEMOUNT	0 – 100 ppm +/- 1 ppm	1 sec	15 min

Results and Discussion

NH_3 emissions averaged at 130 g d^{-1} LU^{-1} and 120 g d^{-1} LU^{-1} during the two fattening periods in spring and at 97 g d^{-1} LU^{-1} and 94 g d^{-1} LU^{-1} in the summer period and in the winter period, respectively. The total variation of the mean daily NH_3 emission rate was in a range of 54 to 181 g d^{-1} LU^{-1} or 5 to 26 g d^{-1} pig^{-1} and thus comparable to the upper range of mean values reported in literature for fattening pigs, kept on fully or partly slatted floors (23 to 150 g d^{-1} LU^{-1} or 5 to 20 g d^{-1} pig^{-1}; Aarnink (1997); Keck (1997); Groot Koerkamp et al. (1998); Ni (1998); Hahne et al. (1999); Heber et al. (2000); Navarotto et al. (2000); Rom and Dahl (2002); Vranken et al. (2002); Demmers et al. (2003); Gallmann (2003); Guarino et al. (2003); Guingand (2003); Van den Weghe et al. (2005). Throughout the whole investigation period, an average emission rate of 5,1 kg NH_3 animal $place^{-1}$ $year^{-1}$ was measured (330 fattening days per year).

The mean diurnal course of the NH_3 emission was mainly influenced by the animal activity, the ventilation rate, and the indoor temperature. Throughout the year, an increase of the daily NH_3 emission rate was pronounced seasonally especially during spring and autumn. In order to compare the ventilation control strategies, days with mean daily outside temperatures below and above 14 °C were considered separately.

Effects of the Ventilation Strategies at Mean Daily Outside Temperatures Below 14 °C

During days with mean daily outside temperatures below 14 °C, only minor influences of the different control strategies on the indoor air temperature and ventilation rate occurred. Average values as well as the total variation of the values were mainly predetermined by the control settings (Table 3 and Table 4). However, the ventilation rate was significantly lowered for the CO_2 controlled ventilation strategy (Strat. C), in average by about 20 % compared to the Reference (Table 3). Thus, the mean indoor temperature of Strat. C was increased by about 1 K (Table 4). At mean daily outside temperatures below 14 °C, water fogging was mainly used for increasing the relative humidity on an inter-quartile range of 51 % to 61 % (Strat. B and Strat. A), compared to 44 % to 52 % (Reference). When using Strat. C, however, water fogging was additionally applied to support indoor air cooling.

Table 3. Ventilation rate [$m^3 h^{-1} pig^{-1}$] at mean daily outside temperatures below [>T1<] and above 14 °C [>T2<]

	Reference	Strat. B	Strat. C	Strat. A
mean >T1<	45^{b}	46^{b}	36^{a}	46^{b}
Inter-quartile range	31 – 51	34 – 55	29 – 40	34 – 56
mean >T2<	**119^{c}**	**93^{b}**	**80^{a}**	**92^{b}**
Inter-quartile range	120 – 131	65 – 127	57 – 100	67 – 117

$^{a, b, c}$ means with different superscript letters differ significantly (p < 0,05)

Table 4. Indoor temperature [°C] at mean daily outside temperatures below [>T1<] and above 14 °C [>T2<]

	Reference	Strat. B	Strat. C	Strat. A
mean >T1<	$19{,}2^{a}$	$18{,}8^{a}$	$19{,}9^{b}$	$18{,}9^{a}$
Inter-quartile range	16,6 – 21,0	17,3 – 20,2	18,6 – 21,4	17,9 – 20,1
mean >T2<	**$24{,}5^{c}$**	**$20{,}4^{a}$**	**$21{,}8^{b}$**	**$20{,}4^{a}$**
Inter-quartile range	21,3 – 27,5	18,4 – 22,2	19,4 – 23,2	18,6 – 21,9

$^{a, b, c}$ means with different superscript letters differ significantly (p < 0,05)

Considering NH_3 emissions during mean daily outside temperatures below 14 °C, the three ventilation strategies based on humidifying (Strat. B, Strat. A; Strat. C) featured significantly, in average 10 % to 14 % higher NH_3 emissions when compared to the reference strategy (Table 5). As the evaporation rate of the fogged water depends largely on indoor temperature and humidity (Haeussermann et al., 2005), an incomplete evaporation of the fogged water during cold and humid or during moderate warm days was likely to cause humid and subsequent fouled surfaces. The relation between pen fouling and the release of NH_3 or the NH_3 emission rate is reported among others in Aarnink (1997), Ni (1998) and Gallmann (2003). According to Aarnink and Elzing (1998), an increase in pen fouling causes an increase in the percentage rate of NH_3, released from the floor surface, from 30 % towards up to more than 40 % of the total NH_3 release.

Table 5. NH_3 emission rate [$g d^{-1} LU^{-1}$] at mean daily outside temperatures below [>T1<] and above 14 °C [>T2<]

	Reference	Strat. B	Strat. C	Strat. A
mean >T1<	99^{a}	113^{b}	109^{b}	113^{b}
Inter-quartile range	84 – 113	87 – 142	82 –125	90 – 140
mean >T2<	**114^{b}**	**110^{b}**	**113^{b}**	**110^{b}**
Inter-quartile range	86 – 131	77 – 138	100 – 121	79 – 128

$^{a, b, c}$ means with different superscript letters differ significantly (p < 0,05)

Effects of the Ventilation Strategies at Mean Daily Outside Temperatures Above 14 °C

Clear influences of the ventilation control strategies on the ventilation rate and indoor air temperature occurred at mean daily outside temperatures above 14 °C. Here, the ventilation rate was reduced in average by about 22 % when using the fogging system (Strat. B and Strat. A). The combination of adiabatic indoor air cooling and a partly CO_2 controlled ventilation rate (Strat. C) did furthermore result in a reduction of the mean ventilation rate by about 33 % (Table 3). Comparing mean daily outside temperatures below and above 14 °C, the indoor temperature was approximately 1.5 K to 5.3 K higher at the latter, whereof the total difference was depending on the ventilation strategy (Table 4). Due to evaporative indoor air cooling (Strat. B, Strat. C, and Strat. A), diurnal temperature peaks were lowered in maximum by about 7 K, in average in >T2< by about 4 to 5 K. When using the fogging system, the inter-quartile range of the relative indoor humidity was increased on 64 % to 82 % (Strat. B, Strat. A, and Strat. C).

Based on the significantly reduced ventilation rate and indoor temperature, a reduction of the NH_3 emission rate was expected for those ventilation strategies which cool the indoor air by fogging of water. However, no significant differences occurred between the mean NH_3 emission rate of the different ventilation control strategies at mean daily outside temperatures above 14 °C (Table 5). A seasonal influence on the NH_3 emission rate was indicated by the significant differences between mean daily outside temperatures below and above 14 °C of the reference ventilation. However, an increase of the NH_3 release, caused by incomplete evaporation of the fogged water, and subsequently fouled surfaces, has to be assumed also for mean daily outside temperatures above 14 °C. Thus, the reduction of the NH_3 emission rate due to the lowered ventilation rate and lowered indoor temperature can be estimated approximately with 10 % to 14 %, but has to take into consideration all multiple influences. Resulting from the investigations, the reduction of the indoor temperature and ventilation rate was sufficient to counteract an increased NH_3 emission rate, caused by incomplete evaporation and fouled surfaces. Nevertheless, the reduction of emitting NH_3 from animal facilities by evaporative indoor air cooling would require furthermore an optimisation of the fogging control with regard to an continuously complete evaporation of the water.

Conclusions

The influences of ventilation control (ventilation rate and indoor temperature), and adiabatic indoor air cooling on the emission of NH_3 were investigated in a research pig facility throughout four fattening periods. The following conclusion were drawn:

- The yearly emission rate averaged on 5,1 kg NH_3 animal place^{-1} year^{-1} (330 fattening days);
- The mean diurnal course of the NH_3 emission rate was mainly influenced by the animal activity, the ventilation rate, and the indoor temperature;
- Throughout the year, an increase of the mean daily NH_3 emission rate was pronounced seasonally especially during spring and autumn;
- NH_3 emissions were increased for ventilation strategies with humidifying at mean daily outside temperatures below 14 °C. For warmer outside temperatures, however, this increase was counteracted by the clear reduction of the indoor temperature and ventilation rate;
- The potential to reduce NH_3 emissions from mechanically ventilated pig facilities by the reduction of the indoor temperature and ventilation rate can be estimated with 10 % to 14 % during mean daily outside temperatures above 14 °C;
- Nevertheless, in order to realize this reduction potential for NH_3 emissions, using evaporative indoor air cooling, an optimisation of fogging control, with regard to an continuously complete evaporation of the water was required.
- Due to the effect of the fogging system and incomplete evaporation of water on the NH_3 emission rate, no estimation of separate effects of temperature or ventilation rate can be concluded from these investigations.

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Emissions of Particulate Matter (PM_{10}) from Housing Systems for Fattening Pigs

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Abstract

Indoor and exhaust concentrations of aerosols with an upper particle size limit of 10 µm (PM_{10}) were measured discontinuously during two fattening periods. The investigation were performed in a research pig facility, equipped with a mechanical under-floor ventilation system. Continuous measurements included indoor temperature, humidity, ventilation rate, and animal activity. Indoor and exhaust concentrations of airborne dust were sampled discontinuously during full day periods. For the measurements, calibrated scatter light photometers (TSI, Model DustTrak 8520) has been used. Measuring frequency was 1 minute. Thereby, the correlation between the indoor and exhaust PM_{10} concentration was generally high, featuring an R^2_{adj} of 0.82. Nevertheless, for low ventilation rates during winter, only 65 % of the aerosols, measured indoors, were transported to the outside, while for high ventilation rates in summer, the percentage between indoor and exhaust concentrations was clearly increased on 95 %. Similarly, the mean PM_{10} emission rate was increased from 4.2 g d^{-1} LU^{-1} in winter towards 7.2 g d^{-1} LU^{-1} during the summer period.

Introduction

The release of dust particles in animal husbandry is influenced mainly by feeding operations, used bedding materials, animals (particles from skin and excrements), as well as the kind of ventilation and management (Aarnink et al., 1999; 2004; Hartung, E. et al., 2004; Keck et al., 2004). It is well known that aerosols and bioaerosols in animal husbandry can cause respiratory health problems (Donham et al. 1995, Seedorf and Hartung, J. 2002). Thus, possibilities to influence the indoor dust concentration in pig husbandry has been investigated intensively during the last years (CIGR, 1994; Pedersen et al., 2000). Nevertheless, only few information about ranges of particulate emissions in relation to season, husbandry systems or regions exists. High ventilation rates during summer are accompanied in general with low indoor concentrations but increased emission rates, especially of inhalable and PM_{10} particle size fractions (Takai et al., 1998; Aerts et al., 2004; Jacobson et al., 2004; Koziel et al., 2004).

Methods

Indoor and exhaust concentrations of PM_{10} aerosols were measured discontinuously during two fattening periods (Haeussermann et al., 2006). The investigations were performed in a research pig facility (Hartung, E., 2001), equipped with a mechanical ventilation system (Figure 1). The two compartments of the research facility featured two pens each, 27 pigs per pen, and were equipped with a slotted concrete floor and a slurry pit underneath each pen. Fresh air was supplied via two air inlet pore channels per compartment, the outgoing air was extracted under-floor (Figure 1). Feeding was supplied either liquid, using a sensor feeding system (20 feeding times per day), or ad libitum using a mash feeding system. Straw was offered via an occupation equipment.

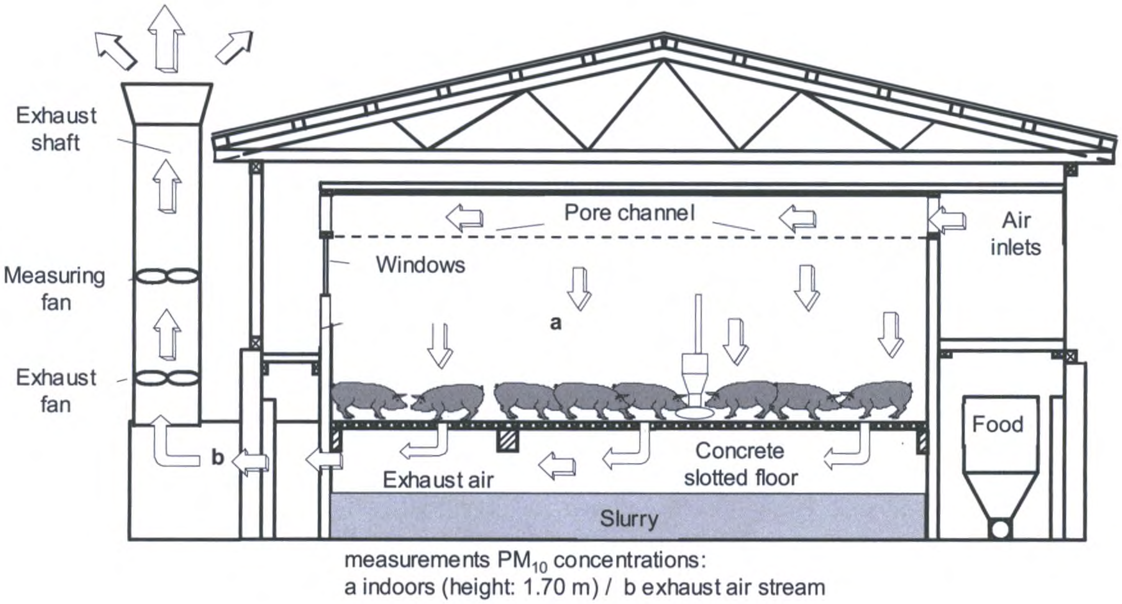

Figure 1. Vertical projection of the research facility for fattening pigs (modified, adopted from Hartung, E. 2001; Gallmann, 2003)

Measurements

Continuous measurements included ventilation rate, indoor temperature, humidity, and animal activity (Table 1). Airborne PM$_{10}$ particles (particles < 10 µm) were monitored discontinuously during full day periods, simultaneously at one representative measuring point indoors as well as in the exhaust shaft (Figure 1). For the PM$_{10}$ measurements, calibrated scatter light photometers were used (Table 1). The measuring frequency for dust, ventilation rate, indoor temperature, humidity, and animal activity was one average value per minute. The average weight of the animals was determined every three weeks and was interpolated for time periods in between.

Table 1. measured variables, measuring instruments, frequencies and accuracies

	Measuring instrument	measuring range / accuracy	measuring frequency
Ventilation rate	measuring impeller MULTIFAN	200 – 10000 m³/h +/- 20 m³/h	1 min
Air temperature	resistance (PT 100) Hygroclip, ROTRONIC	- 40 to + 85 °C +/- 1 °C	1 min
Relative humidity	capacitive Hygroclip, ROTRONIC	0 – 100 % +/- 1 %	1 min
Animal activity	passive infrared sensors (Pedersen and Pedersen, 1995)	0 – 5 V (scale)	1 min
PM$_{10}$	Scatter light photometer TSI, DustTrak 8520™	0,001 – 100 mg m^{-3} +/- 0,001 mg m^{-3}	1 min

Results

The correlation between the indoor and exhaust PM$_{10}$ concentration was generally high, featuring an R^2_{adj} of 0.82 (0.89 and 0.61 in winter and summer, respectively, Figure 2). Nevertheless, for low ventilation rates during winter, only 65 % of the aerosols, measured indoors, were transported to the outside, while for high ventilation rates in summer, the percentage between indoor and exhaust concentrations was clearly increased on 95 %. Similarly, the mean PM$_{10}$ emission rate was increased from 4.2 g d^{-1} LU^{-1} in winter (mean ventilation rate: 291 m³ h^{-1} LU^{-1}) towards 7.2 g d^{-1} LU^{-1} during the summer period (mean ventilation rate: 735 m³ h^{-1} LU^{-1}) (Table 2). Beside ventilation, the level of the emission rate was influenced to a high range by the animal weight and animal activity. Nevertheless, relations between influencing variables and the PM_{10} emissions, as well as between indoor and exhaust concentrations, differ at different housings and husbandry systems. Hence they have to be investigated separately for each individual system.

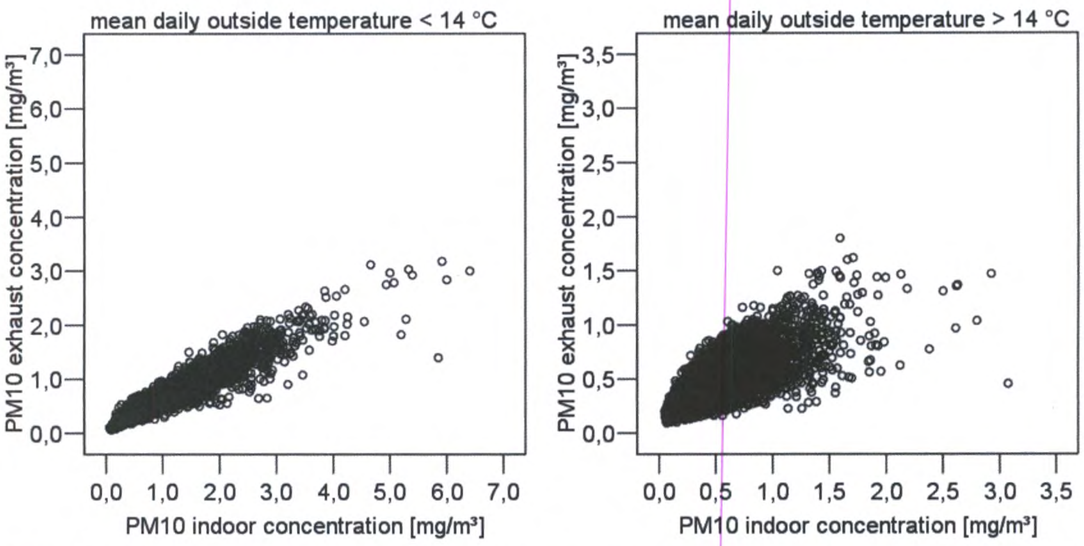

Figure 2. range diagrams of the PM_{10} indoor and exhaust concentration during the winter and summer period (mean daily outside temperature below and above 14 °C, respectively)

Table 2. Average ventilation rate, PM_{10} concentration and PM_{10} emission during the winter and the summer period

	Ventilation rate [m³/h/LU]	PM_{10} indoor concentration [mg/m³]	PM_{10} exhaust concentration [mg/m³]	PM_{10} emission rate [g/d/LU]
Winter period (t_o < 14 °C)	**291** (235 – 372)	**1.03** (0,57 – 1,26)	**0,58** (0,37 – 0,79)	**4,2** (3,3 – 5,2)
Summer period (t_o < 14 °C)	**735** (598 – 854)	**0.44** (0,35 – 0,56)	**0,43** (0,30 – 0,67)	**7,2** (5,5 – 9,5)

t_o: mean daily outside temperature (): total range (mean values separate measuring periods)

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Using Physical Models to Simulate Emissions from Anaerobic/Facultative Swine Manure Stabilization Ponds

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Abstract

Researchers at Oklahoma State University (OSU) have simulated emissions from swine manure stabilization ponds under controlled conditions using a pilot bioreactor consisting of four 270 liter, 3.66 m deep columns that recreate environmental conditions found in anaerobic/facultative lagoons. The pilot bioreactor was equipped with both head-space and wind-tunnel air sampling devices. When fed manure produced by hogs eating a typical corn-soybean diet and programmed to simulate late summer conditions, the pilot bioreactor showed that 65% of applied carbon was emitted as CH_4 and CO_2, and 72 % of applied nitrogen was emitted as NH_3. There was a marked difference in the CH_4:CO_2 ratio between night and day emissions, with higher ratios occurring during the night. NH_3 emissions greatly increased during daylight hours once the temperature of the liquid surface began to rise.

Introduction

Most manure handling systems found on swine farms in the southern United States use anaerobic stabilization ponds – commonly called lagoons -- to treat liquid manure. Effluent is recycled to the buildings to remove manure, and excess effluent is irrigated to cropland. Stabilization ponds are low labor, easily managed treatment systems, and are very efficient at removing organic matter from the waste stream (Hamilton et al, 2002). The overall effect of lagoon treatment is to covert organic matter to gases. Emitted gases are byproducts of the carbon, nitrogen, and sulfur cycles of the pond ecosystem, and include the problematic gases: methane (CH_4), carbon dioxide (CO_2), hydrogen sulfide, oxides of nitrogen, and ammonia (NH_3).

The complexity of making measurements of full-scale stabilization ponds is a major factor in the limited availability of lagoon emission data in the literature. The difficulty arises from two hindrances: the ability to study cause and effect relationships under controlled conditions, and the ability to accurately measure emission of gases over the entire lagoon surface (Hamilton et al, 2006). Researchers at Oklahoma State University (OSU) have attempted to overcome these hindrances by constructing a pilot bioreactor consisting of four 270 l, 3.66 m deep columns that recreate environmental conditions found in anaerobic/facultative lagoons. By precisely controlling the environmental (heating, lighting, mixing) and operational conditions of the column section, cause and effect relationships can be explored. The problem of surface measurement is reduced by assuming that the layered biological communities found in lagoons can be recreated in the 3.66 m of column depth, and that the gases emitted from the top of this column represent emissions from the total lagoon surface.

Results and Discussion

The model pilot bioreactor used in this study is made of four insulated PVC pipes, 0.305 m (1 ft) in nominal diameter, and 3.66 m (12 feet) in depth. Hamilton (1998) gives a complete description of bioreactor design. Two sets of two columns are coupled with the same lighting and heating systems to achieve two replicated sets of conditions from the four columns. Columns are labeled A, B, C, and D; and are usually operated as two, two-column sets (AB and CD). The pilot facility was inoculated with effluent and sludge from a facultative lagoon located at the OSU Swine Research Center (OSU-SRC) in the fall of 1998, and has been programmed ever since to repeat the heating, mixing, and lighting patterns experienced by a typical anaerobic/facultative stabilization pond under late-summer conditions at 35° N latitude in Oklahoma. Swine manure fed to the pilot bioreactor was collected from pigs housed in metabolic chambers fed a fortified corn-soybean. Two distinctly different lagoon systems have been modeled using the pilot bioreactor.

Single-Cell Anaerobic Stabilization Simulation

Two single cell anaerobic lagoons, operated at organic loading rates typical of lagoons found on commercial swine farms have been monitored on an annual basis for a study of sludge accumulation (Hamilton, 2004). These lagoons, labeled OK1 and OK2 were used to set organic loading rates on the pilot scale simulator. EC and pH of the-full sized stabilization ponds were used to compare the response of loading rate and hydraulic balance of the pilot-scale bioreactor to full-sized lagoons. Both of the full-sized lagoons used in this study remained red or violet-red in color year round, which indicates the presence of photosynthetically active, purple sulfur and/or purple non-sulfur, anaerobic bacteria. Scum layers of windblown algae also frequently occurred in downwind corners of the lagoons. The bioreactor columns also maintained a red to red-violet color under a thin layer of algae. Algae were removed from the surface every day before feeding.

Table 1. Geometric data and organic loading rates of one pilot-scale bioreactor column and single cell anaerobic stabilization ponds (from Hamilton et al, 2006).

Facility	Dimensions at Maximum Drawdown Level (m)				Side-slope	Volumetric Loading Rate (g VS/m^3-day)	Surface Loading Rate (kg VS/ha-day)
	Depth	Dia.	Width	Length			
Pilot Bioreactor	3.66	0.305	-	-	-	25.2	935
OK1	2.22	-	36.3	65.1	2.7:1	67.6	1,160
OK2	2.29	-	37.4	61.0	3.5:1	61.0	922

Emission rates of CH_4 and CO_2 from the lagoon simulator were measured using a closed chamber system. The atmosphere immediately above the liquid surface was covered by a modified version of chamber used by Ball et al. (1999) for soil analysis. The chamber used in this study was a 0.2 m tall, 0.09 m diameter polypropylene (Nalgene) cylinder, held in a floating position by a block of 0.15x0.15 m-square Styrofoam. Working headspace of the gas collecting cylinder was 800 ml. Samples were taken from the floating chamber on a frequent basis and analyzed on a gas chromatograph. Daily mass of CH_4 and CO_2 emitted was calculated by multiplying the molar emission rate by the time interval over which it was measured, and summing masses for all the measurement intervals for the day.

Average values of CH_4+CO_2 gas emission rate and average values for molar CH_4:CO_2 ratios are plotted against time of day in Figure 1. CH_4+CO_2 emission was relatively constant at 2 mmoles/m^2-min, with a slight increase after feeding, and a slight decrease after the lights were turned off. Mixing produced a spike in gas emission at 7:00. There was a remarkable difference in CH_4:CO_2 ratio between day and night. The ratio of CH_4 to CO_2 dropped from 1.8 to 1.2 almost immediately after the lights turned on, and returned to 1.8 after the lights went off.

Daily carbonaceous gases masses emitted are given in Table 2. Average mass of CH_4+CO_2-C emitted was 2,400 mg/day. The mass of total carbon applied to the column was 3,750 mg/day; therefore, approximately 65% of the applied carbon is accounted for in CH_4+CO_2 emission.

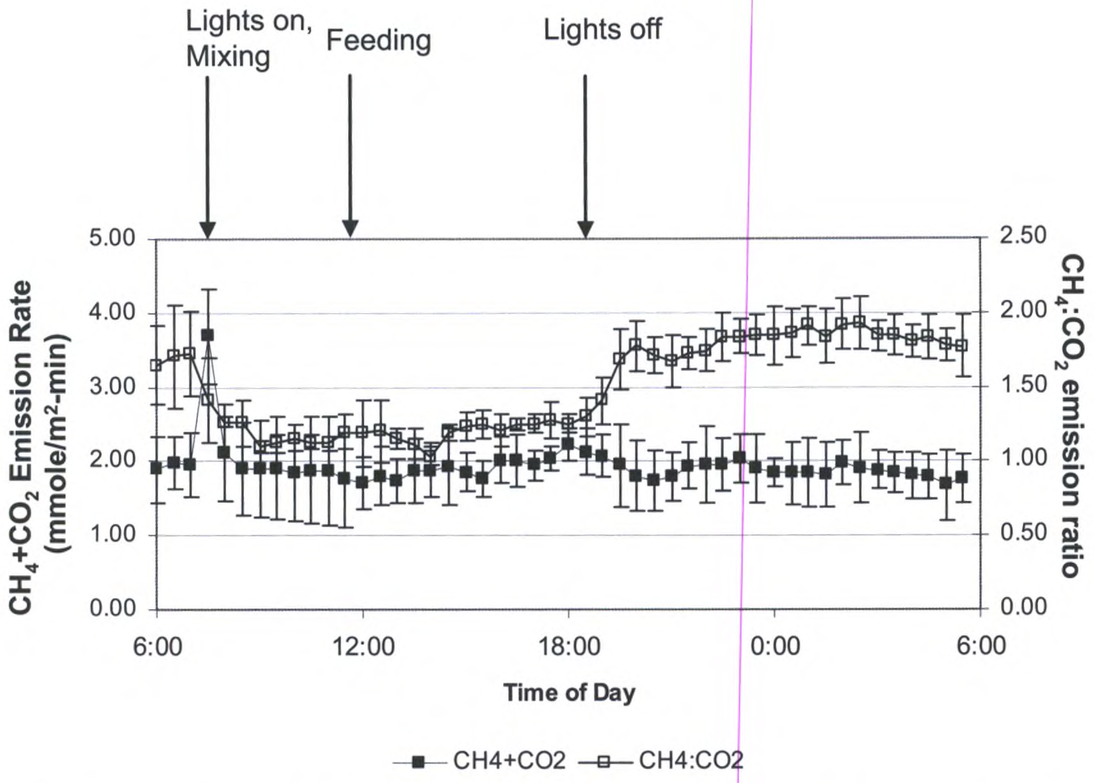

Figure 1. Emissions of carbonaceous gases from pilot reactor simulating single-cell, anaerobic stabilization ponds (from Hamilton, 2006).

Table 2. Masses of Methane, carbon dioxide, and total carbon emitted from pilot reactor simulating single cell anaerobic swine manure stabilization ponds during 24 hour test periods (from Hamilton et al, 2006).

	June 22/24	July 17-18	August 10-11
Moles emitted (mmole/day)			
CH_4-C	140	125	91
CO_2-C	94	89	61
CH_4+CO_2-C	234	214	152
Masses emitted (mg/day)			
CH_4	2,200	2,000	1,450
CO_2	4,100	3,900	2,700
CH_4+CO_2-C	2,750	2,550	1,800
Masses emitted from an equivalent lagoon surface (kg/ha-day)			
CH_4	300	280	200
CO_2	580	550	380
CH_4+CO_2-C	390	360	260

Facultative Stabilization Pond Simulation

The stabilization pond located at OSU-SRC differs from lagoons typically found on commercial hog farms in Oklahoma. First, the surface organic matter loading rate of the OSU-SRC lagoon is considerable lower than those found at commercial facilities (Table 3). Secondly, the physical set-up of the OSU-SRC waste stabilization pond makes it function somewhere between a single-cell and a two-cell lagoon. Manure enters the smaller of two cells. This is called the "Sludge Side" because settled manure solids are retained in the cell by the 1.35 m high, submerged dike. Liquids are free to pass into a larger "Clear Side". There is considerable mixing of liquids between the two cells due to wind action and the water level increase of the sludge side during loading. In effect, the lagoon acts like a two-cell lagoon for manure solids, and a single cell-lagoon for lagoon liquids. The pilot bioreactor was set-up so that liquids are allowed to pass from the outside side column (A or D), which simulates the sludge side, to the inside column (B or C), which simulates the clear side. Only the outside column was fed. Liquids taken 2 m deep from both columns were recycled to the top of the two-column set at 7:00 each day.

EC and pH of the pilot-scale bioreactor was comparable to the full-sized stabilization pond. Both the bioreactor and the full-sized pond remained red or violet-red throughout the experiment. Furthermore, community DNA extracted from the bioreactor columns had a 70% match to community DNA extracted from the analogous positions in OSU-SRC pond (Ball et al, 2006).

Table 3. Loading rates on the OSU-SRC lagoon and a two-column set of the pilot-scale bioreactor.

Facility	Volumetric Organic Loading Rate "Clear Side" only (g VS/m^3-day)	Surface Organic Loading Rate across Total Surface (kg VS/ha-day)	Surface Nitrogen Loading Rate across Total Surface (kg TKN/ha-day)
Pilot Bioreactor	24	169	26
OSU-SRC Stabilization Pond	77	355	27

Methane, carbon dioxide, and ammonia emissions were measured by placing wind tunnel on top of each column. Air speed across the top of the 0.071 m^2 column section was 0.2 m/s. NH_3 gas concentrations (ppb by volume) were determined by sampling the wind tunnel flow with a chemiluminecence ammonia analyzer. A gas chromatograph was placed in line with the ammonia analyzer to determine CH_4 and CO_2 concentrations.

The 26 kg TKN/ha loading rate given in Table 3 translates to 360 mg of N applied to the two-column set each day (25 mmoles/day). Emissions of carbonaceous gases and NH_3 from the simulated facultative stabilization pond are given in Table 4. From this table, approximately 72% of applied nitrogen was captured as NH_3 from the facultative pond.

Table 4. Average mass of carbonaceous and ammonia gasses emitted (mmole/day), simulated facultative stabilization pond under late summer conditions (from Carter and Hamilton, 2005).

	CH_4	CO_2	Total C	NH_3
Sludge Side	110	90	200	11.0
Clear Side	50	30	80	7.6
Total	160	120	280	18.6

The ratio of CH_4 to CO_2 did not exhibit as great a difference between night and day as was exhibited in the simulation of the single-cell anaerobic lagoons, and CH_4+CO_2 emissions were higher that would be expected for the lower VS loading rate. These discrepancies may be explained by the constant air flow across the surface of the simulator. The actual situation is likely to be a combination of both results in that air flow across the surface of a stabilization pond will cycle between periods of calm and wind. NH_3 emissions showed a profound difference between night and day, and appear to coincide with the temperature of the liquid surface. As temperature rises, so does emission of NH_3.

Conclusions

Simulation of anaerobic/facultative stabilization ponds under late summer conditions show that 65 % of applied C and 72 % of applied N can be accounted for in the emission of CH_4, CO_2, and NH_3. CH_4 emissions from the simulated stabilization ponds were comparable to those of similarly loaded swine manure treatment lagoons (Hamilton, et al, 2006; Sharpe and Harper, 1999).

The pattern of CH_4 to CO_2 ratio may be attributed to a combination of four processes: (i) aerobic and anaerobic photosynthetic organisms, and aerobic bacteria living symbiotically with aerobic photosynthetic organisms, produce higher volumes of CO_2 during daylight, (ii) the small, but appreciable amount of oxygen produced by algae during daylight suppresses CH_4 production, (iii) higher volumes of CO_2 are produced as complex organic matter is converted to acetate by both aerobic and anaerobic bacteria, and (iv) excess CO_2 and H_2 are converted to CH_4 by methanogenic bacteria once acetate reserves become depleted. NH_3 emission patterns tend to be less complex, and are tied to surface temperature of lagoons.

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Reducing the Risks of Pesticide Exposure via Atmospheric Transport

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Abstract

The fate and transport of agriculturally-significant organic pollutants in the atmosphere is an important national issue. Volatile components and residues bound to dusts may rise into the atmosphere, travel long distances, and be deposited far from the point of origin through various deposition processes, risking contamination of sensitive ecosystems. Examining the environmental fate of agricultural pesticides is complicated by their sporadic and intense application to soils and crops throughout the growing season. Scientists at USDA-ARS have worked with their partners to conduct fundamental research on the atmospheric transport and deposition of semi-volatile organic pesticides at field, watershed, and regional scales. Results analysis of these will assist in identifying the major volatilization pathways from which more effective management practices to mitigate pesticide volatilization can be developed.

Introduction

Research concerning the environmental fate and transport of semi-volatile organic pollutants has focused largely on urban/industrial chemicals such as polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs). In many cases, these chemicals are present at equilibrium in the atmosphere, and their fate may be predicted using models based on partition coefficients. The study of the environmental fate of agricultural pesticides is complicated by their sporadic and intense application to soils and crops throughout the growing season. Agricultural pesticide residues are rarely present at equilibrium concentrations within the environmental compartments of soil, plants, air and water. They are structurally more complicated and have more reactive sites compared with industrial pollutants; thus, they are frequently more polar and will degrade more readily and at variable rates. Long term studies have been conducted on the atmospheric transport and deposition of non-fumigant organic pesticides at field, watershed, and regional scales and a number of new phenomena have been documented.

Methods

Air samples were obtained using a high volume sampler with a glass-fiber filter followed by polyurethane foam plugs. Vapor concentrations were measured periodically for 24 h in the regional studies and continuously for up to 120 h after pesticide application usually in a logarithmic profile above the soil surface in the field studies. Rain samples collected on an event-basis and extracted on-line using SPE cartridges. All samples were analyzed by GC/MS or by LC-MS-MS as were appropriate blanks and spikes. In nearly all studies, weather towers were located near samplers.

Results and Discussion

Several field studies were conducted to examine the processes that affect pesticide volatilization and deposition. While losses from the soil to the atmosphere were greatest within the first 24 hours after application, volatilization continued to be an important loss mechanism. The magnitude and duration of post-application pesticide volatilization was enhanced by high soil moisture and solar radiation (temperature), frequent light precipitation events, and low organic carbon soils (Prueger et al., 2005). These volatilized residues were readily transported to adjacent riparian areas and captured by the plant canopy.

Subsequently, precipitation events washed off the plant canopy and delivered the residues directly to surface waters via the riparian ecosystem streams, bypassing mitigation by the riparian area. These observations are being incorporated into tools for predicting the effectiveness of riparian mitigation function (Angier et al., 2002; 2004).

Studies of regional deposition via precipitation have shown that the Henry's constant of the pesticide will strongly influence its persistence in the atmosphere. Chemicals with low Henry's constants will be readily scavenged, and frequent precipitation events after application will result in increased wet deposition loads. Chemicals with higher Henry's constants will be less efficiently scavenged and loads will correspond to total rainfall during the entire growing season. In a four year study of the Choptank Watershed on the Chesapeake Bay, wet deposition was shown to contribute up to 20% of the annual pesticide loadings to the Bay. In addition, the net gas-exchange flux for some compounds was found to be both positive and negative, i.e., pesticides can be both deposited to and volatilized from the Bay waters depending on the time of year. Particle phase deposition also contributed to the total atmospheric contributions; however, traditional particle phase partitioning, as described by the Junge-Pankow model, cannot explain the higher pesticide concentrations observed on the particles (Goel et al., 2005; Kuang et al., 2003).

In South Florida, the Everglades and Biscayne National Parks are in close proximity to agricultural fields. The effects of high humidity, warm temperatures, low soil organic carbon, frequent pesticide application and crop irrigation, as is the case for South Florida, create a unique situation whereby atmospheric concentrations of pesticides would be expected to be quite high. Indeed, air concentrations in South Florida ranged from 1 to 3 orders of magnitude higher than is typically observed in other places in the country. Pesticide concentrations in rain were also higher. However, pesticide concentrations in canal waters were below levels of concern suggesting that either degradation in the water or a net pesticide flux from the water to the air may be occurring (Hapeman et al., 2003; Harman-Fetcho et al., 2005).

Ecosystems at high altitudes and located downwind from agricultural regions are particularly vulnerable to atmospherically-derived pesticide residues. Large quantities of pesticides are used in the San Joaquin Valley. Warm, moist prevailing winds from the coastal mountains remove volatilized residues from the agricultural fields and deposit them in the much cooler Sierra Nevada Mountains. This long range transport has been implicated as contributing to the amphibian population declines. In addition, the colder temperatures will decrease pesticide degradation rates increasing the pesticide residue exposure times for especially for aquatic species (Fellers et al., 2004; Lenoir et al., 2000; Sparling et al., 2001).

Overall, pesticide residues are present in the atmosphere throughout the year. Deposition occurs continuously via particulate and gas phase deposition. The new knowledge acquired over the course of these investigations will be useful in the development of more effective management practices to mitigate pesticide volatilization. Prevention of volatilization is the most efficient way reduce atmospheric deposition loads and to lessen the impact of agricultural activities on their surrounding ecosystems.

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Assessment of Crop Loss Due To Cumulative Air Pollution Load in South West MP, India

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Abstract

The present research is unique in the sense; as for the first time the cumulative air pollution load in an area was taken into account for the crop loss and not the individual pollutants, that too in field conditions at 5 sites. In an attempt to identify the extent of the distribution of SPM, SO_2, NO_X and O_3 at certain sites in South West M.P. Air monitoring following standard protocol (APHA,1977) was carried out. The areas were classified in two types on the basis of class of pollutant i.e. one where particulate pollutants were higher i.e. Nayagaon-Khor and Nimbaheda and another where gaseous load was prevalent i.e. Dewas, Nagda and Pithampur. Crop samples were also collected from same sites for analysis of biomass, yield and calorific value. The annual SPM loads in the area ranged between 204 - 459 mg/m^3 at about 1km and 79 - 154 mg/m^3 at 5km. The new industrial areas however had lower load but the cement zone of Nayagaon-Khor and Nimbaheda retains as high as 259 mg/m^3 at 5km. As regards SO_2, the annual average was between 5 44 mg/m^3 with about 36 44 mg/m^3 in most of the regions at 1km distance except the cement zone (5mg/m3). The levels remain 15 - 20 mg/m^3 between 4 5 km and up to 5 mg/m3 at 7 - 8 km in prevailing direction of wind. Almost similar conditions existed for NO_X where annual average concentration ranged up to 52 mg/m3 with a minimum level of 17 mg/m3 between 4 - 5 km. The range of O_3 levels remained between 9 - 32 mg/m^3 at 1km in prevailing wind direction. But the range of cumulative load of all these pollutants was too high in the host zone of 1 - 2 km around the industrial pockets i.e. 218 - 618 mg/m^3 and remained as much as 302 mg/m^3 at about 5 km. In prevailing wind directions these levels extend up to 6 - 8 kms or more. Quantitatively and qualitatively crops were affected due to cumulative pollution load and percentage reduction in biomass at all sites ranged between 6 - 25% while in the yield 10 - 35% reduction was observed. The calorific value also indicates the impact of cumulative pollution load. About 5 - 35% decrease was noted. Also regression analysis among all these parameters with cumulative pollution load indicates a direct relationship.

Characterization and Abatement of Air Emissions from Egg Production

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Introduction and Objectives

Air pollutants including ammonia (NH_3), particulate matter (PM), odor, and pathogens, emitted by animal production represent risks to the health and well-being of animals, workers and neighbors, and to the global environment (NRC, 2003). This project, funded by the 2004 USDA-NRI program, will provide information about air emissions from layer facilities, since egg production is known to emit significant amounts of PM, ammonia and odor. Specifically, the objectives of the monitoring are to:

1. Determine whether belt battery (BB) barns emit less air emissions than high rise (HR) barns and establish emission factors for each type of barn.
2. Quantify effects of litter composting and wet scrubbers on air emissions.

Test Methods

Emission measurements will be conducted for 12 months at an egg production facility that has BB barns, HR barns, and chicken manure composting sheds. One on-farm instrument shelter (OFIS) will monitor two BB barns and the other OFIS will monitor two HR barns. A portable ammonia monitoring unit (PAMU) will monitor wet scrubber performance for three months.

A multi-point gas sampling system in each OFIS will continuously cycle gas analyzers through six or seven sampling locations in each barn. Real-time PM monitors will measure PM_{10} and $PM_{2.5}$. Weather, barn temperature and humidity, bird and worker activity, and operation of fans, feeders, lights, and manure belts will be recorded along with PM and gas concentrations every 60 s. Pathogen (E. Coli, Salmonella) and odor (European olfactometry) emissions will be measured monthly. Manure sampling and nitrogen (N) balance analysis will be conducted to analyze ammonia N losses.

Differential static pressure across walls with ventilation fans and conveyor openings will be measured continuously. A vibration sensor will be attached to the shroud of each exhaust fan to monitor individual fan operation. Fan airflow rate will be estimated based on barn static pressure, fan operation time, and the relationship between static pressure and fan airflow rate. Emissions will be calculated by multiplying the concentration differences between inlet and exhaust by barn ventilation rate. Continuous data will be acquired at 1 Hz and a 60-s average recorded every minute.

Air at selected continuous or nearly continuous exhaust fans will be sampled for 10 min per measurement cycle and ambient air will be sampled for 30 min/day to measure NH_3 and carbon dioxide (CO_2) concentrations. PM_{10} and $PM_{2.5}$ concentrations will be measured continuously at one fan exhaust in each of the BB and HR barns (Figs. 1 and 2). Each month, pathogen and odor concentrations will be sampled, and manure N will be analyzed to calculate the N balance.

The characteristics of each barn and compost shed are given in Table 1. Each BB barn has eight tiers (5 upstairs and 3 downstairs) in each of six rows of cages. Each barn is equipped with 24 end-wall fans (divided into four groups of six fans each located in the four corners), and 12 fans in each sidewall. The diameter of these 48 fans are 122 cm. A 122-cm single-speed fan in the NE conveyor belt annex and a 92-cm fan in the SW annex are used to keep the manure belts warm with exhaust barn air (Fig. 1). The gas sampling locations are allocated to the fans associated with ventilation stages 1 and 2, which are distributed along the length of the building.

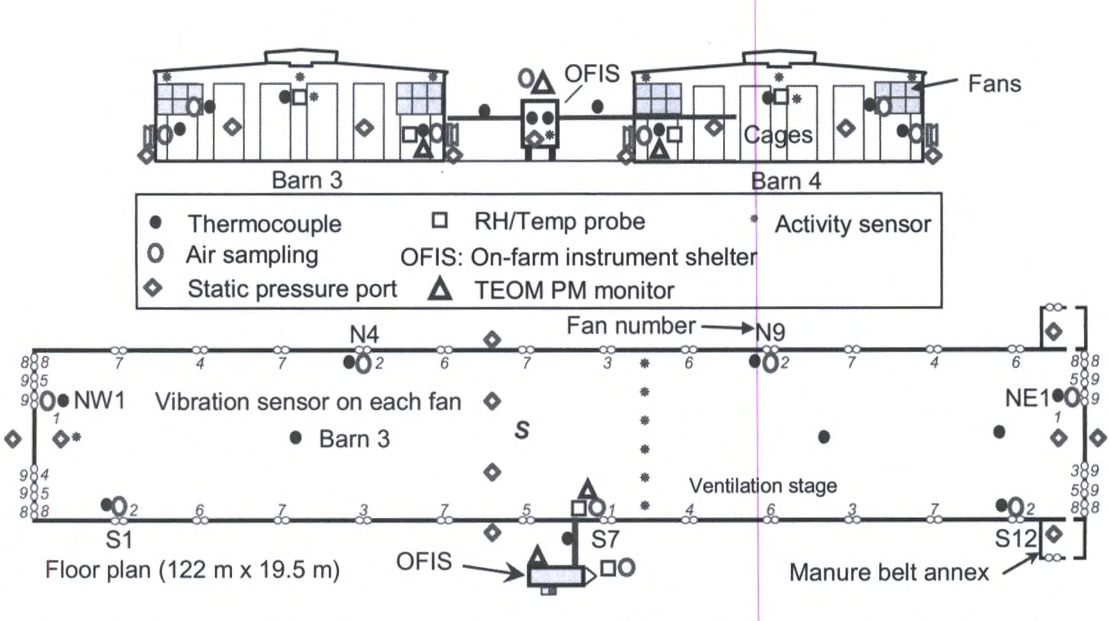

Figure 1. End view and floor plan of BB barns and OFIS. Barn 4 floor plan not shown.

Each HR barn has 8 rows of 8-tier cages. The barns are equipped with ridge baffle air inlets and sixteen, 122-cm diameter exhaust fans in each sidewall of the manure pit (Fig. 2). The fan staging strategy proposed to accommodate the gas sampling locations has ventilation stages 1-3 controlling the three sampled fans in each pit sidewall.

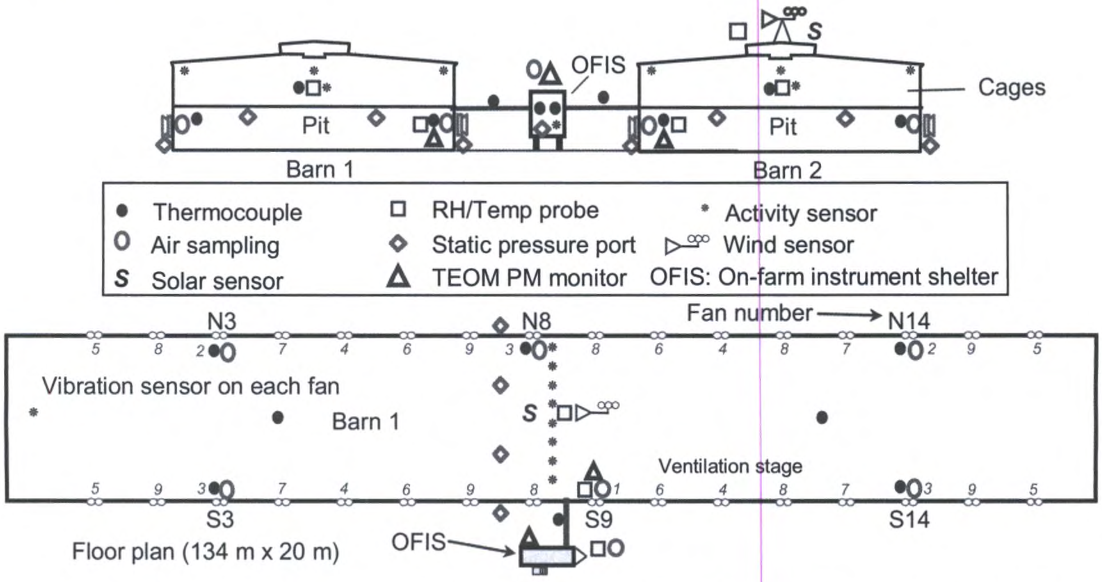

Figure 2. End view and floor plan of HR barns and OFIS. Barn 2 floor plan not shown.

The compost piles in the compost shed are turned every 3 d. There are four single-speed 92-cm diameter ventilation fans in the east endwall. A wet scrubber will be installed at the exhaust of one of these fans to test its ammonia removal efficiency. Ammonia and carbon dioxide concentrations will be sampled at the inlet (fan exhaust) and outlet of the wet scrubber.

Measurement Innovations

Fan airflow measurement is a challenge, especially in large barns with 30 to 100 fans. Based on the concept of using a commercial vibration detector to monitor fan operation (Ni *et al.*, 2005), a new low-cost (about $28 each) vibration sensor was developed and tested by the Ohio State University. It provides low-voltage on/off fan signals, is weatherproof, and is more reliable than the commercial detector.

Purdue University developed a new multi-point gas sampling system (GSS) that is more reliable and easier to maintain than previous designs. The GSS temperature is higher than ambient temperature to reduce risk of condensation and decrease gas adsorption and desorption at wetted surfaces. Additional sensors in the new GSS allow better monitoring and control.

Data acquisition and control software for barn air emission measurements, AirDAC, written in LabVIEW (National Instrument, Austin, TX), has been significantly improved. AirDAC is now more user-friendly and allows easy modification of configurations such as sampling locations, and records all configuration and parameter changes in a file.

A detailed Quality Assurance Project Plan (QAPP) for this project is being written in conjunction with the QAPP for the National Air Emission Monitoring Study (NAEMS) (Heber 2006), which has many common standard operating procedures.

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Table 1. Characteristics of Barns at Egg Production Site.

Descriptive Parameters	Barns 3-4	Barns 1-2	Shed 2
# buildings at site	4	4	2
Building type	BB	HR	Hoop
Year of construction	1996	1975	1996
Building orientation	E-W	E-W	E-W
Spacing between buildings, m	18.3	12.8	18.0
Width, m	19.5	19.8	18.9
Length, m	122	134	107
Ridge height, m	8.5	7.5	4.6
Sidewall height, m	6.1	6.7	3.6
Barn inventory	180,000	138,000	-
Number of tiers of cages	8	6	-
Manure collection method	Belts	Loader	-
Manure accumulation time, d	4	365	60
External storage	Shed	-	-
Duration of external storage, d	100	-	-
Number of air inlets	12	8	4
Inlet type	Ridge baffle	Ridge baffle	Door
Inlet control basis	Temperature	Temperature	-
Walls with fans (N,S,E,W)	N,S,E,W	N,S	E
Number of exhaust fans	50	32	4
Largest fan diameter, cm	122	122	91
Smallest fan diameter, cm	70	122	91
# ventilation stages	6	8	-
# temperature sensors	16	8	-
Summer cooling	Air	Misters	-

Nitrous Oxide Fluxes from Loamy Sand Soil in Northeast Germany - Seasonal Variations and Influence of Nitrogen Fertilization, Precipitation, and Crop Types

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Abstract

N_2O flux measurements have been carried out at an experimental field since 1999. Different types and levels of fertilization were applied to annual plants (hemp, rape, rye, sorghum, triticale) and perennial plants (grass, poplar, willow). The mean of annually accumulated emission of N_2O-N from all measuring spots was 1.4 kg N_2O-N ha^{-1} y^{-1} and the mean annually fertilizer-induced N_2O-N emission from all fertilized sites was 0.6 % for the period from 1999 to 2005. The mean nitrogen conversion factor for perennial crops was lower (0.3 %) than that for annual crops (0.8 %). Several enhanced N_2O emission spots with maxima above 1000 μg N_2O m^{-2} h^{-1}, lasting for several weeks, were observed at sites with 150 kg N ha^{-1} y^{-1} fertilization in the course of the measurements. These local peak emissions were mainly responsible for the dependence of the nitrogen conversion factor on fertilization level. Annual N_2O emissions are correlated to annual precipitation. Soil nitrate concentrations and N_2O emissions show similar seasonal variations. Usually during the winter season, increased N_2O fluxes due to freeze-thaw cycles were measured for a few days. Additionally, four non-fertilized sites of fallow land were studied in 2002, the year with the highest precipitation of the study period. The comparatively high emission rate of 5.3 kg N_2O-N ha^{-1} y^{-1} of this fallow land should be the result of three emission enhancing factors: mineralisation of plant cultivation residues in the soil (hemp in 2001), soil cultivation in 2002 (plowing and harrowing to get a "black fallow"), and higher denitrification rate due to increased water-filled pore space in 2002.

Introduction

Nitrogen fertilizing is one of the main sources of anthropogenic contribution to the global dinitrogen oxide (N_2O) emission as shown by Bouwman (1990), who found a linear relationship between N_2O emissions and fertilizer input. In soil, N_2O is produced predominantly by two microbial processes, the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-; called nitrification) and the reduction of NO_3^- to gaseous forms NO, N_2O, and N_2 (called denitrification). The rate of N_2O production depends on the availability of mineral N in the soil (e.g. Granli and Bøckman, 1994; Bouwman, 1996). The conversion factor (ratio of N_2O-N emission to input of fertilizer-N) ranges from 0.25 % to 2.25 % depending on soil type (IPCC, 1996 and 2000). When the cultivation of crops is assessed with regard to greenhouse gas abatement, this conversion factor plays a significant role, e.g. the nitrogen fertilizer-induced emission of N_2O-N may counterbalance the carbon dioxide (CO_2) advantage of biofuels (in case of high nitrogen fertilizer application and conversion factor > 2 %), since N_2O as a greenhouse gas contributes to global warming 296 times more effectively than CO_2 (IPCC, 2001).

This aspect, to know more details on this possibility of counterbalancing the CO_2-advantage of biofuels, was the motivation to start a long-term study on N_2O soil emissions, the results of which are presented here. In 1993, the German Federal Environment Office (Umweltbundesamt: UBA) published an ecological balance of rapeseed oil and of rapeseed oil methyl ester (UBA, 1993). This publication led to an intensive discussion about the emission of N_2O and the quantities of nitrogen fertilizer that are really necessary for the cultivation of renewable raw materials. This UBA study reached the controversial result that, with regard to the impact on the climate, rapeseed oil as a diesel substitute does not provide substantial advantages as compared with diesel fuel. The environmental effects of the fertilizer-induced N_2O emissions are an important buttress of the argumentation chain, since a fertilizer-induced N_2O-N emission of 2% to

3% of the annual quantity of N fertilizer applied was assumed to be the probable range. Therefore, several institutions in Germany started studies with the aim of better quantification of the nitrogen conversion factor under climatic conditions of Central Europe.

Later on, in a second UBA study on the assessment of the use of rapeseed oil/RME in comparison with diesel fuel (UBA, 1999), the conversion factors recommended by the IPCC (1996, 2000) were employed. N_2O formation remained as a negative factor in the environmental balance. With regard to the greenhouse effect, the CO_2 balance was now positive, but only additional CO_2 credits due to the comprehensive utilization of rape biomass give biofuel a real advantage over diesel fuel. In addition, nitrous oxide contributes to the depletion of ozone in the stratosphere and thus exerts a negative influence on the environmental balance of biofuels. Since N_2O release is controlled by many factors, significant deviations may occur depending on the location.

Agronomic practices such as tillage and fertilizer applications can significantly affect the production and consumption of N_2O because of alteration in soil physical, chemical, and biochemical activities. Following N-fertilizer applications, an increase in N_2O flux rates has been observed in field and laboratory experiments (e.g. Jackson, 2003; Kaiser et al., 1998; Mulvaney et al., 1997). N_2O emission from croplands at site scales occurs essentially with great spatial and temporal variability (Dobbie and Smith, 2003; Hellebrand et al., 2003; Veldkamp and Keller, 1997). The annual pattern of temporal variation of N_2O emissions is determined in the temperate regions by the seasons and weather conditions, since soil N_2O emissions are regulated by temperature and soil moisture and so are likely to respond to climate changes (Frolking et al., 1998).

In addition to this background variability, agricultural management such as tillage and fertilizing schedule may enhance N_2O emission (Hénault, 1998a and 1998b). Tillage could cause immediate changes in microbial community structure reported by Jackson et al. (2003), thus produce large N_2O emissions at the beginning of crop season. Spatial variability is mainly caused by heterogeneity in soil properties and agricultural management. Additionally, there are different short time emission peaks lasting for hours or days and weeks, the source of which is not explicitly known (Brown et al., 2002; Dobbie and Smith, 2003; Hellebrand et al., 2003; Van der Weerden et al., 1999; Veldkamp and Keller, 1997).

Nitrification and denitrification processes may be stimulated after the application of nitrogen fertilizer (e.g. Dobbie et al., 1999; Firestone and Davidson, 1989; Freney, 1997; Mosier, 1994). The balance between the two processes contributing to the N_2O emission will vary with climate, soil conditions and soil management (Skiba and Smith, 2000). Soil cultivation and precipitation, affecting the soil air exchange rate, should also influence nitrification and denitrification, which are aerobic and anaerobic processes, respectively. Numerous authors studied the emission of N_2O dependent on soil type, fertilization and crop species (e.g. Flessa et al., 1998; Dobbie et al.; 1999; Hénault et al., 1998a). There are still uncertainties regarding the soil specific conversion factor, especially the influence of precipitation, soil moisture, temperature, soil nitrate concentration and other variables. Since the N_2O emission factor depends on local conditions, the main aim of this study was to determine this factor and its typical variability for the cultivation of annual and perennial crops on sandy soils under climatic conditions of North-East Germany.

Methods

Experimental Field

The N_2O flux measurements have been performed since 1999 in an experimental field with various crops cultivated for the production of biofuels. The experimental field was established in 1994. A sufficient homogeneity of the soil is reflected by means and standard deviations (sd) of 40 soil samples (soil horizon 0 to 30 cm): clay content 6.2 % (sd: 1.3), organic carbon content.

Table 1. Plants at the columns of the experimental field since 1999.

Each column consists of 4 differently fertilized sites: A, B, C, and D.

Column Period	1	2	3	4	5	6	7	8	9	10
10/1998-03/1999	**G***	**W***	P1	**P2****	P3	F	T	R1	T1*	F*
04/1999-09/1999	**G***	**W***	P1	**P2****	P3	H1	T	R1	T1*	H2*
10/1999-03/2000	G*	W*	P1	P2**	P3	R1	T	H1*	F*	H2
04/2000-09/2000	G*	W*	P1	P2**	P3	R1	T	H1*	Ra*	R1
10/2000-03/2001	G*	W*	P1	P2**	P3	T2	T	R4*	F	G,C
04/2001-09/2001	G*	W*	P1	P2**	P3	T2	H1	R4*	H1	G,C
10/2001-03/2002	G	W*	P1	P2**	P3	R2*	F*	Rc*	H1	G,A,C
04/2002-09/2002	G	W*	P1	P2**	P3	R2*	F*	Rc*	H1	G,A,C
10/2002-03/2003	G	W*	P1	P2**	P3	T2*	Rb*	R2*	H1	G,A,C
04/2003-09/2003	G	W*	P1	P2**	P3	T2*	Rb*	R2*	H1	G,A,C
10/2003-03/2004	G	W*	P1	P2**	P3	Rb*	R3*	T2*	H1	G,A,C
04/2004-09/2004	G	W*	P1	P2**	P3	Rb*	R3*	T2*	Co	S
10/2004-03/2005	G	W*	P1	P2**	P3	F*	T2*	R2*	F	F
04/2005-09/2005	G1	W*	P1	P2**	P3	H1*	T2*	R2*	S*	SF*
10/2005-03/2006	G1	W*	P1	P2**	R5*	R6*	R7*	R2*	F	F

*:	Columns with one measuring spot per site A, B, C, and D.
**:	Columns with two measuring spots per site A, B, C, and D.
A:	Alfalfa (*Medicago sativa)*
C:	Clover (*Trifolium repens*)
Co:	Corn (*Zea mays*)
F:	Fallow land
G:	Grass (orchard grass: *Dactylis glomerata* L.)
G1:	Sudan grass (*Sorghum sudanense*)
H1:	Hemp (*Cannabis sativa* L.) var. Felina 34
H2:	Hemp (*Cannabis sativa* L.) var. Fedrina 74
P1:	Poplar *(Populus maximowiczii x* P. nigra) var. Japan 105 with grass
P2:	Poplar *(Populus maximowiczii x* P. nigra) var. Japan 105
P3:	Poplar *(Populus maximowiczii x* P. trichocarpa) var. NE 42 with grass
Ra:	Rape (*Brassica napus* L. spp. oleifera Metzg.) var. Licosmos
Rb:	Rape (*Brassica napus* L. spp. oleifera Metzg.) var. Express
Rc:	Rape (*Brassica napus* L. spp. oleifera Metzg.) var. Artus
R1:	Rye (*Secale cereale* L.) var. Amilo
R2:	Rye (*Secale cereale* L.) var. Matador
R3:	Rye (*Secale cereale* L.) var. Avanti
R4:	Rye (*Secale cereale* L.) var. Hacada
R5:	Perennial Rye (*Lolium parvifolium* L.) var. Waldi
R6:	Perennial rye (*Secale montanum* L.) var. Permonta
R7:	Rye (*Secale cereale* L.) var. RPM 1
S:	Sorghum (pearl millet: *Pennisetum glaucum* (L.) R. Br.) var. Rona 1
SF:	Sunflowers (*Helianthus annuus* L.) var. KW0411
T:	Topinambur *(*Jerusalem artichoke: *Helianthus tuberosus* L.)
T1:	Triticale (X *Triticosecale* Wittm.) var. Alamo
T2:	Triticale (X *Triticosecale* Wittm.) var. Modus
W:	Willow *(Salix viminalis)* with grass

0.9 % (sd: 0.14) and pH value 6.0 (sd: 0.34). Soil texture of the topsoil was classified as loamy sand (Hellebrand and Scholz, 2000). The weather means at the Potsdam Weather Service station (about 10 km away) between 1951 and 1980 were 8.6 °C for air temperature and 595 mm for precipitation. In the period of this study (1999-2005), the mean temperature increased (mean of the last seven years: 9.7 °C) and the mean annual precipitation decreased (mean of the last seven years: 573 mm; DWD, 2006).

The field was subdivided into 40 sites (624 m^2 each). Different plant varieties (Tab. 1) or plant combinations were arranged as columns (four sites each, labeled as A, B, C, and D) with a distance of 6 m between each column. Grass (column 1) was mowed two to three times every year. The short rotation wood (or "field wood": poplar and willow; column 2 to 5) was periodically harvested (every two to four years). The crops in columns 6 to 10 were mostly annual plants, which were rotated or planted according to actual needs. The different types and levels of fertilization were applied in four rows, perpendicular to the columns. There were sites with different levels of nitrogen input (fertilizer: calcium ammonium nitrate; A: 150 kg N ha^{-1} y^{-1}; B and C: 75 kg N ha^{-1} y^{-1}) supplemented by PK-fertilizer (A), wood ashes (B), and straw ashes (C) and sites without fertilization (D).

Gas flux Measurements

In 1997 and 1998, FT-IR gas analysis was applied (Hellebrand and Scholz, 2000). FT-IR gas analysis gave variation coefficients of 7% for N_2O and CH_4 flux measurements at atmospheric mixing ratios and of up to 20% for NH_3 concentration determination below 1 ppm. Therefore, the accuracy was insufficient to get precise nitrogen conversion factors. Nevertheless, it could be shown that no NH_3 was emitted, although calcium ammonium nitrate was applied as fertilizer.

Since 1999, gas flux measurements have been performed four times a week by means of closed chamber technique and an automated gas chromatograph (GC). The sealing rings (Y profile, sealing by water level) for the gas flux chambers (cover boxes) were embedded in the soil. One ring was put on each measuring spot at the sites A to D of the columns with different crops. The gas flux chambers had a volume (V) to area (A) ratio of $V/A = 0.315$ m (volume 0.064 m^3, inner diameter 0.509 m). Fluxes were usually measured in the morning. Two evacuated gas samplers (100 cm^3 bottles with Teflon sealing and vacuum taps) were connected to each box. The first was filled when the box was put on the water-sealed ring on the soil and the second one after about 60 minutes enclosure time. The samplers were then connected with the automated GC-injection control system. The GC was fitted with an electron capture detector (ECD). The operating temperature for the ECD was about 300 °C (sometimes manual shifted up to ±5 K to get identical peak sizes for the maximum concentrations of CO_2 and N_2O of the calibration gases mixture) and the column temperature was 65 °C. Both the pre-column (length 1 m) and the main column (length 3 m) were packed with Porapak Q (80/100 mesh). In one computer-controlled run up to 64 samples could be analyzed. The N_2O detection limit was 5 ppb (5×10^{-9}). At atmospheric mixing ratio, the coefficient of variation was 1.2 % for N_2O measurements. For each level of fertilization, the N_2O emission factor was calculated by taking the difference between the mean values of the fertilized sites and the non-fertilized sites.

CO_2 and N_2O, both of them generated in the soil, have nearly equal diffusion constants. The easily measurable CO_2 served for the evaluation of linearity and mixing homogeneity of the measuring chamber (measurements at several heights in the closed chamber). Studies on the concentration increase of CO_2 in a flux chamber on bare soil and on grass sites demonstrated that the increase in concentration was linear (R^2 between 0.9973 and 0.9986) during measurement periods of 60 minutes (Hellebrand and Scholz, 2000).

Soil Ion Measurements

Since 2003 soil samples were drawn from sites with the three fertilizer levels (A: 150 kg N ha^{-1} y^{-1}; B: 75 kg N ha^{-1} y^{-1} and D: no fertilizer) and different crops (columns 2, 4, 6, and 7; Tab. 1). The samples were taken from the 0-30 cm soil depth close to the corresponding measuring rings. The water content of the soil samples was obtained by gravimetric determination of weight loss when soil samples were dried at 105 °C for 24 h. The concentration of mineral nitrogen (ammonia nitrogen NH_4^+-N and nitrate nitrogen NO_3^--N) and other ions was determined by ion chromatography after extracting by deionized water and filtering. In the present paper, only the course of concentration of soil nitrate is considered. The detailed evaluation of all the soil ion concentrations will be published elsewhere.

Results and Discussion

Fertilizer-Induced N_2O Emissions

The emission of N_2O followed the expected pattern of fertilizer-induced emissions (FEE in Fig. 1 and Fig. 2, fertilization date in Tab. 2). These enhanced emissions were detectable at all fertilized sites after fertilizing and lasted from four to eight weeks. We also found temporarily and spatially limited high fluctuations throughout the entire study since 1999. N_2O emission peaks over 1000 µg N_2O m^{-2} h^{-1} were observed from few measuring spots (Fig. 2). These findings are in accordance with other studies (e.g. Augustin et al., 1998; Röver et al., 1998). Because measurements were taken four times a week, the "regularities" (induced emissions) and fluctuations could be studied with sufficient temporal resolution at different crop sites on a relatively homogeneous sandy soil. Except during the few freeze-thaw cycles (FTC in Fig. 1 and Fig. 2), the N_2O emission rate usually dropped to less than 30 µg N_2O m^{-2} h^{-1} between October and March.

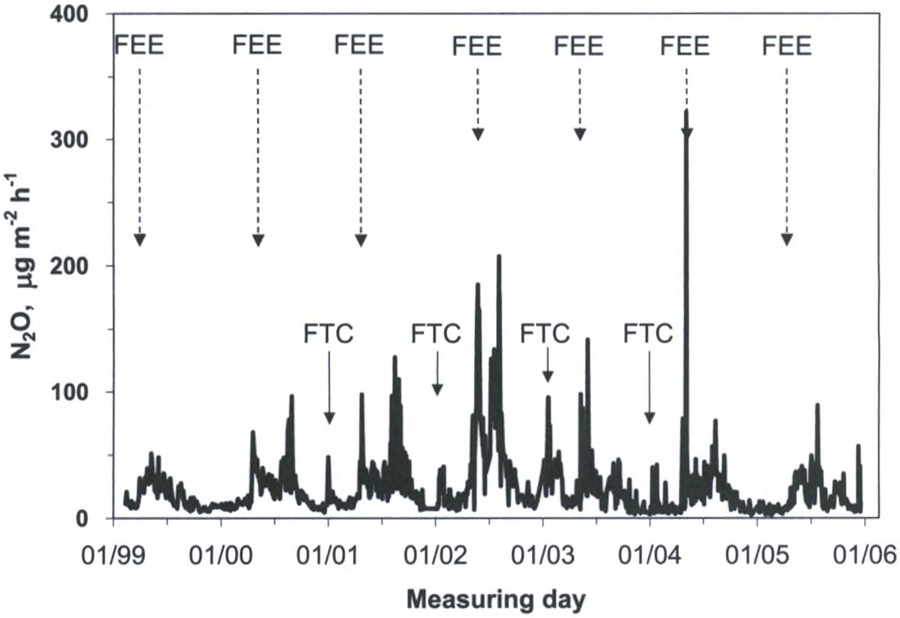

Figure 1. Time series of N_2O emissions from all sites of the experimental field.
Daily mean values of emission rates from all measuring spots,
FEE: Fertilizer enhanced emissions, fertilisation usually in April, see Table 2,
FTC: Freeze thaw cycle enhanced N_2O emissions, usually in January.

Table 2. Date of fertilizer application and fertilization rates.

Year	1999	2000	2001	2002	2003	2004	2005
Fertilization							
1*	March 26	April 14	April 17	April 9	April 8	April 21	April 18
2**	May 7	May 5	May 7	May 13	May 14	May 6	May 10
3***	May 18	May 25	May 14	May 21	June 2	May 18	May 19

1* : A: 50 kg N ha^{-1} y^{-1}; B: 50 kg N ha^{-1} y^{-1}; C: 50 kg N ha^{-1} y^{-1}; D: -
2** : A: 50 kg N ha^{-1} y^{-1}; B: 25 kg N ha^{-1} y^{-1}; C: 25 kg N ha^{-1} y^{-1}; D: -
3***: A: 50 kg N ha^{-1} y^{-1}; B: -; C: - D: -

Other Enhanced N_2O Emissions

No clearly frost-induced emission rates were found in January 2000 and 2005. Frost-induced N_2O-emissions are related to the course of temperature and could be dependent on several factors such as groundwater level, water-filled pore space, soil pH, soil nitrate content, soil texture, and soil structure (Flessa et al., 1998; Röver et al., 1998; Mogge et al., 1996). However, the frost-induced emissions we measured at a couple of the sites are small compared to the total annual N_2O emission budget from the sandy soil of the experimental field.

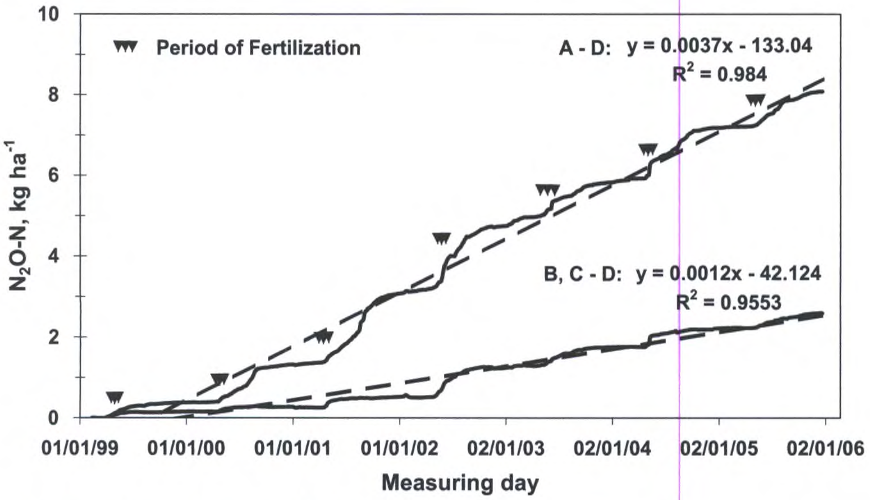

Figure 3. Accumulated mean emission differences.
The regression line of the mean emission differences between A-sites (150 kg N ha^{-1} y^{-1}) and D-sites (non-fertilized) has a threefold slope compared to the mean emission differences between B/C-sites (75 kg N ha^{-1} y^{-1}) and D-sites.

There were several unusual high emission periods at fertilized sites within the course of the measurements since 1999. In 2000, emission rates between 400 and 800 µg N_2O m^{-2} h^{-1} were measured at the rape site with fertilization level of 150 kg N ha^{-1} y^{-1} from the end of July till to the harvest in the beginning of September. In 2001, very high N_2O emission rates of up to 1370 µg N_2O m^{-2} h^{-1} were observed from one poplar measuring spot with fertilization level of 150 kg N ha^{-1} y^{-1} over a period from July till October. There were high emission rates between 350 and 900 µg N_2O m^{-2} h^{-1} from all fertilized rape sites for several weeks in July 2002 and in July 2004. Since most of these enhanced emissions were observed at A-sites (150 kg N ha^{-1} y^{-1}), the conversion factor increases with the fertilization rate (Tab. 3 and slope of regression lines in Fig. 3).

Additionally, four non-fertilized sites of fallow land were measured in 2002. High emission rates between 200 and up to 1480 µg N_2O m^{-2} h^{-1} were observed from the sites of the fallow land during the period from end of May 2002 till middle of August 2002. This fallow land, which was cultivated and fertilized the years before, even had the highest annual emission rate of 5.3 kg N_2O-N ha^{-1} y^{-1} although no fertilizer was applied during the year of study. As the fallow land was only ploughed and harrowed in March but no drilled ("black fallow"), the high precipitation in 2002 could have caused enlarged anaerobic zones (increased water-filled pore space) within the topsoil resulting in enhanced N_2O emissions.

Table 3. Annual precipitation, mean N_2O-N emissions and mean nitrogen conversion factor at differently fertilized rows A, B, C, and D.

Year	**Annual Precipitation,** mm	**N_2O-N Emission,** kg N_2O-N ha^{-1} y^{-1}				**N_2O-N Conversion factor,** %		
		Mean of all sites A	Mean of all sites B, C	Mean of all sites A, B, C	Mean of all sites D	Mean of all sites A	Mean of all sites B, C	Mean of all sites A, B, C
1999	406.1	1.11	0.84	0.88	0.71	0.26	0.20	0.22
2000	537.8	1.92	0.88	0.98	0.80	0.75	0.17	0.37
2001	626.8	2.47	0.86	1.09	0.74	1.15	0.32	0.59
2002	762.5	2.80	1.34	2.15	1.10	1.13	0.86	0.95
2003	428.3	1.92	1.23	1.40	0.84	0.72	0.64	0.66
2004	630.2	1.78	0.86	1.15	0.48	0.86	0.70	0.75
2005	617.1	1.61	0.95	0.85	0.54	0.71	0.48	0.56
1999-2005	**572.7**	**1.94**	**1.13**	**1.41**	**0.86**	**0.72**	**0.55**	**0.60**

Table 4. Mean N_2O-N emissions and conversion factors from sites with perennial crops and annual crops (differently fertilized rows A, B, C, D).

	N_2O-N Emission, kg N_2O-N ha^{-1} y^{-1}				**N_2O-N Conversion factor,** %		
Crop	A	B	C	D	Mean sites A	Mean sites B, C	Mean sites A, B, C
Grass (3 years)	1.30	0.97	1.23	1.04	0.17	0.08	0.11
Willow (6 years)	1.04	0.75	0.97	0.57	0.31	0.39	0.36
Poplar (7 years)	1.72	0.68	0.89	0.50	0.82	0.38	0.52
Mean Perennial crops	**1.35**	**0.80**	**1.03**	**0.70**	**0.43**	**0.28**	**0.33**
Rye (6 years)	2.68	1.38	1.67	0.93	1.16	0.79	0.91
Triticale (4 years)	2.09	1.70	1.44	0.74	0.90	1.11	1.04
Hemp (2 years)	1.29	0.78	0.99	0.67	0.41	0.29	0.33
Rape (4 years)	3.82	1.66	2.02	1.40	1.61	0.59	0.93
Mean Annual crops	**2.48**	**1.38**	**1.53**	**0.94**	**1.02**	**0.70**	**0.80**

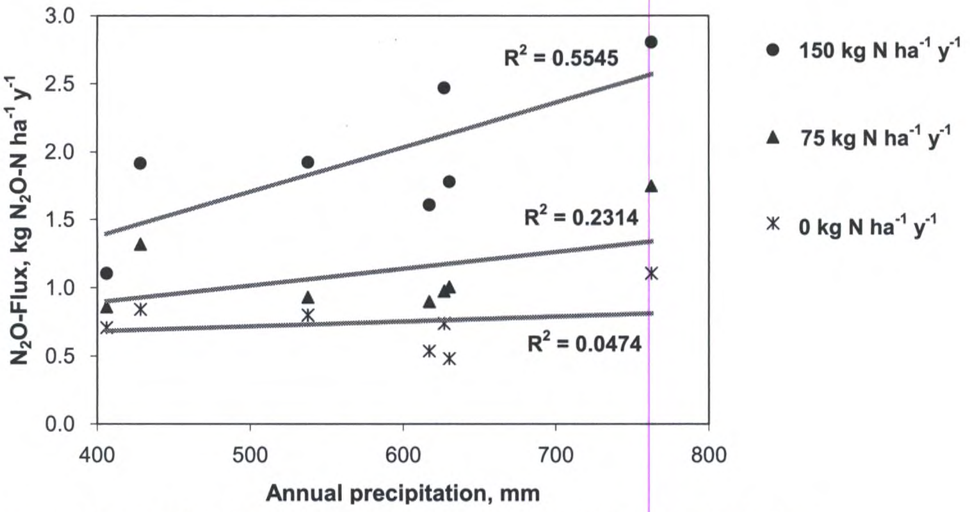

Figure 4. Correlation between mean annual total N_2O emissions from differently fertilized sites and annual precipitation.

The mean annual N_2O emissions and the mean nitrogen conversion factor of the differently fertilized rows A, B, and C had maxima in the period 2001/2002 (Tab. 3). There is a clear correlation between annual precipitation and annual total N_2O emissions. This correlation increases with the level of fertilization (Fig. 4). An obvious difference exists between N_2O emission rates from sites with perennial crops and annual crops (Tab. 4). The emissions from sites with annual crops were about 50 % higher than from sites with perennial crops. This is true, independent on fertilization level. Considering the conversion factor, it was about twice for sites with annual crops compared to perennial crops (Table 4). Although this phenomenon is not fully understood, changes in physical structure by soil tillage may alter biological activity and thus N_2O emission over the crop season (Jackson, 2003; Kaiser et al., 1998; Mulvaney et al., 1997).

Soil Nitrate and N_2O Emissions

The correlation between soil nitrate and N_2O emissions was much lower then initially expected. The close relationship between N_2O generation and extractable soil nitrate (denitrification) and ammonia (nitrification) is well understood (e.g. Bremner, 1997). The seasonal change of soil nitrate concentration and N_2O fluxes shows similarities (Fig. 5), but due to the temporal and local fluctuations of N_2O emissions and of nitrate concentrations, the correlation might depend on the locations and schedule of soil sampling compared to the N_2O flux measurements. The soil samples were taken outside the measuring rings (in order not to disturb the soil surface) in distances of 30 to 50 cm, neither synchronous nor daily but only weekly. There is nearly no correlation between daily flux measurements and weekly nitrate concentration measurements ($R^2 = 0.03$), whereas a slight correlation exists for the monthly means ($R^2 = 0.20$). This is interpreted as a result of the high dynamics of N_2O flux, which can considerably vary at the same measuring ring in the course of one week. On the other hand, the monthly means reflect a general tendency. Therefore, the correlation increases, as both quantities show similar seasonal changes (Fig. 5).

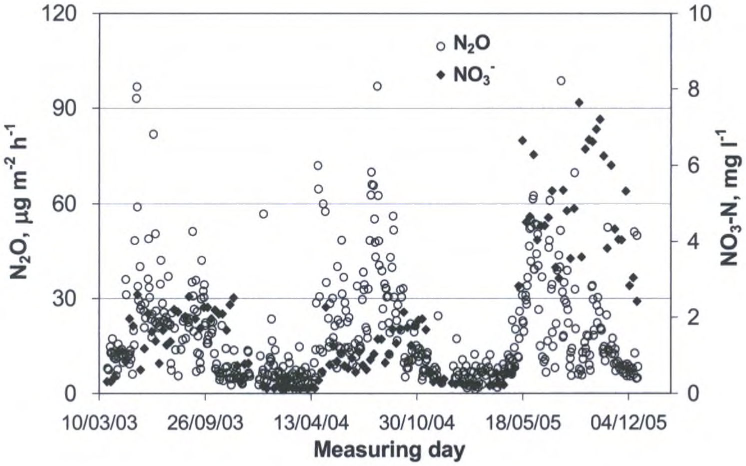

Figure 5. Seasonal change of mean soil nitrate concentration and mean N_20 fluxes

N_2O Emission and CO_2 Mitigation of Energy Crops

The mean N_2O-N emission factor was approximately 0.6 % for all A-, B-, and C-sites (0.7 % for A-sites and 0.5 % for B- and C-sites) for the year period from 1999 to 2005 (Tab. 3). Additionally, the emission factor shows variation depending on crop type (annual or perennial) and year (precipitation). Due to the local enhanced N_2O emissions from several measuring spots at A-sites, the mean of the emission factor increased with the nitrogen fertilization level (annual means of induced emissions; sites A to B, C; Tab. 3) and annual crops emitted more N_2O than perennial crops (Tab. 4). Reason could be variations in biological activity in dependence on type and level of soil fertilization. This is being examined at present. The results measured here are at the lower part of the range of the N_2O emission factor, which is recommended by IPCC (1996, 2000) for the fertilization-based N_2O inventories. Thus, it can be stated that the emission of N_2O is comparatively low on the sandy soils of our experimental field. The CO_2 advantage of energy crops will not be reduced by nitrogen fertilizing as long as fertilizing results in an adequately higher biomass yield (Scholz and Ellebrock, 2002). This result is also true for other crops, cultivated on sandy soils as source for renewable vegetable raw materials, if excessive fertilizing is avoided.

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Carbon Monoxide from Composting due to Thermal Oxidation of Biomass: An Additional Pathway for CO in Agricultural and Forest Ecosystems

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Abstract

Carbon monoxide (CO) influences tropospheric chemistry and, in particular, tropospheric ozone (O_3) concentration. The major sources of CO are incomplete combustion and photochemical oxidation of atmospheric hydrocarbons. Other sources include emissions from green plants, dry soils, and degrading plant matter. Studying trace gas releases from composting processes with a high-resolution FT-IR spectrometer, we observed emissions of carbon dioxide (CO_2) and CO from heaps of fallen leaves, during rotting of green waste, and windrow composting of livestock waste, and on a laboratory scale, during rotting experiments from non-sterilized as well as from sterilized dead plant matter in a temperature and ventilation controlled substrate container. For composting of green waste, emission rates were calculated from ratios of the concentration differences between compost air and background air and by evaluation of the carbon balance of the heaps. Emissions from windrows of farm waste were measured using gas flux chambers. In laboratory experiments, the plant material was placed in a closed substrate container. In case of experiments with sterilization, the closed container was exposed to 136°C for three hours. After cooling down, the container was ventilated via 0.2 µm filters for concentration analysis. The concentration of CO was up to 120 ppm in compost piles of green waste, up to 10 ppm during composting of livestock waste, and up to 160 ppm during laboratory experiments. The flux ratio of CO-C to CO_2-C varied between 10^{-4} and 10^{-3} during composting and was up to 10^{-2} in experiments with sterilized plant matter. The mean CO flux rates were ~20 mg CO $m^{-2}\ h^{-1}$ for compost heaps of green waste, and 30 to 100 mg CO $m^{-2}\ h^{-1}$ for fresh dung-windrows. Arrhenius-type plot analyses resulted in activation energies of 52 kJ mol^{-1} for thermochemically produced CO from sterilized compost substrate and 65 kJ mol^{-1} for CO from unsterilized compost substrate, i.e. a temperature raise from 5°C to 20°C triplicates the thermal CO production. Though globally and regionally not an important source, thermochemically produced CO emissions could affect local air quality near large composting facilities.

Introduction

The background for CO studies at the Potsdam Institute of Agricultural Engineering

The reunification of Germany in 1990 led to an evaluation of all scientific institutions of the former GDR by the German Science Council with recommendations for future research directions (Wissenschaftsrat, 1991). “Substance cycling and energy fluxes in agriculture” was a new research direction for the Institute of Agricultural Engineering Potsdam-Bornim. With it, the new task for agricultural engineering was now the design of technologies and procedures aiming at greenhouse gas abatement. At the same time (1993), a new federal administrative regulation as part of the German “Waste Avoidance and Management Act”, called “Technical Instruction on Municipal Waste”, was passed (BMU, 1993). Composting became an important way for municipal waste processing by this instruction. Composting has been accepted by the public as an environment friendly way of organic waste processing, but in 1993 there were few figures on the emissions of ammonia (NH_3), nitrous oxide (N_2O), and methane (CH_4) during composting available. Therefore, it was decided to launch research on emissions during composting on a laboratory scale, measurements at pilot plants, and analysis of leaching and emissions from compost heaps in the frame of landscape management and conservation. To analyze the concentrations of NH_3, N_2O, CH_4, and other gases in compost-air, a high resolution FT-IR measuring system was chosen for laboratory studies (Hellebrand and Kleinke, 1996; 1997). Additionally, this system could be used for gas analysis from field measurements by gas sampling with commercial gas bags (Linde, 2006).

During initial evaluation of the recorded FT-IR spectra from compost-air, we observed previously unidentified absorption lines near the intensive CO_2-absorption band (2060-2100 cm^{-1}, Figures 1 and 2). The detailed analysis showed that these lines reflected CO in the mid to high ppm range, which was not expected for green waste compost-air. The compost heaps were located in a clean-air area, far away from traffic lines. The findings of our first evaluation were included in a publication on composting (Hellebrand, 1998). A more detailed search on the sources of CO during composting started, the results of which are presented in this contribution.

CO on a Global Scale

CO is known to the public as an air pollutant and toxic gas. The sources for the atmospheric load results mainly from incomplete combustion of fossil fuels and biomass (1350 Tg; IPCC, 2001a) and photochemical oxidation of atmospheric hydrocarbons (1230 Tg; IPCC, 2001a). Vegetation (150 Tg; IPCC, 2001a) and Oceans (50 Tg; IPCC, 2001a) contribute on a smaller scale. CO is not a greenhouse gas, because its contribution to the infrared absorption in the 10 μm infrared window of the atmosphere is too low. However, emissions of CO have indirect effects on climate through enhanced levels of tropospheric O_3 and CH_4 as a result of its reaction with hydroxyl-radicals HO• (Crutzen, 1974; Liu et al., 1987; Fuglestvedt et al., 1996; Daniel and Solomon, 1998).Therefore, the Working Group I of the Intergovernmental Panel on Climate Change included CO in its reports.

The mean atmospheric CO abundance is approximately 80 ppb, with an atmospheric lifetime of one to three months (IPCC, 2001b). The Northern Hemisphere contains almost twice as much CO as the Southern Hemisphere, mostly due to anthropogenic emissions. Atmospheric CO trends are sensitive to the time period considered, e.g. for the period 1991 to 1999, the CO trend was -0.6 ppb y^{-1}, and for 1996 to 1998, the trend was positive by +6 ppb y^{-1} (IPCC, 2001b). The most important sink for CO is the reaction with HO• (Logan et al., 1981), with a smaller sink via soil uptake (Table 2.6 in IPCC, 1995). The latter results from soil microbial processes (Conrad and Seiler, 1980; Conrad et al. 1981; Conrad and Seiler, 1985a; Scharffe et al., 1990; Conrad, 1996), whereas simultaneously occurring CO production in soils has been assigned to thermochemical oxidation of organic matter (Conrad and Seiler, 1985a; 1985b; Seiler and Conrad, 1987). Although the global budget of CO is fairly well understood, there are some uncertainties associated with the CO fluxes from natural sources.

Direct and Indirect Biogenic Sources of CO

CO from biogenic sources has different pathways – direct CO-release from certain plants (Bauer et al., 1979, and reference therein), production or consumption by specialized microorganisms (Radler et al., 1974; Conrad and Seiler, 1980; 1985a; Conrad, 1988; 1996; Scharffe et al., 1990; King, 1999), generation by photochemical and thermochemical oxidation of biomass (McConnell et al., 1971; Fischer and Lüttge, 1978; Lüttge and Fischer, 1980; Conrad and Seiler, 1985b; Tarr et al., 1995; Kanakidou and Crutzen, 1999; Schade et al., 1999), and by oxidation of CH_4 and of non methane hydrocarbons (NMHC) of biogenic origin, such as isoprene (McConnell, 1971; Crutzen, 1974; Novelli et al., 1992; Miyoshi, et al. 1994).

The production of CO from plant litter (Sanhueza et al., 1994; Zepp et al., 1996 and 1997; Hellebrand, 1998; Sanhueza et al., 1998) in the dark is most likely caused by thermochemical oxidation processes, and has previously been studied in more detail (Schade, 1997; Schade et al. 1999). Thermochemically (or thermally induced) CO production from grass and leaf litter obeys the Arrhenius law with activation energies mostly between 60 and 90 kJ mol^{-1}, with strong evidence that CO is not produced biologically (Schade, 1997; Schade et al. 1999). The authors estimated global CO emissions due to thermochemical oxidation of organic carbon from plant litter of 40 Tg CO (Schade and Crutzen, 1999). Uncertainties are related to the fact that thermal CO production does not only depend on temperature, but also on type of plant litter and moisture content. Increasing moisture content generally promotes CO emission.

Methods

FT-IR Measuring System

Trace gas analysis was carried out with a high resolution FT-IR spectrometer (Spectrum™ 2000, PERKIN ELMER). The system was equipped with two heated, long path multi pass gas cells (FOXBORO® - Invensys Process Systems). The temperature of the cells was kept at 80 °C to avoid condensation at the gold coated mirrors of the cells. The gas cell with optical variable path length of up to 20 m had a measuring volume of 5.4 dm^3 and was used for quantification when samples with at least this volume were available. The second gas cell with a fixed optical path length of 7.2 m (48 passes with a base of 0.15 m) had a volume of only 0.5 dm^3 and was used in experiments with limited sample size or to achieve sufficient time resolution for continuous flow measurements with changing gas composition.

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 a sample spectrum is obtained by a second measurement with gas cell filled. To minimize stochastic and systematic errors the FT-IR spectrometer with its beam channels and detector housings was purged with dry, CO_2 free air (BALSTON® FT-IR Purge Gas Generator; -73°C dew point of cleaned air). Separate MCT-detectors for each gas cell were used to optimize sensitivity. Generally, spectra were recorded with 64 scans.

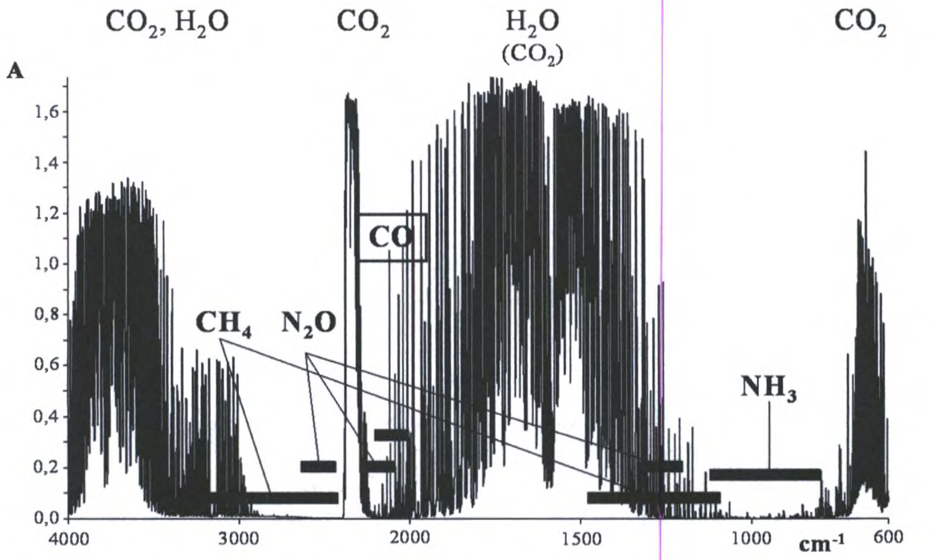

Figure 1. FT-IR spectrum of ambient air between 4000 cm^{-1} and 600 cm^{-1} (absorbance to wave number; measured with 20 m long path gas cell). The IR wave bands of environmentally relevant gases are indicated.

A constant range (4000 cm^{-1} to 600 cm^{-1}) and fixed point intervals (0.05 cm^{-1}) were applied for calibration and for all measurements with quantitative evaluation. The detection limit was better than 10 ppb for CO in nitrogen (20 m gas cell; 0.2 ppm for 7 m gas cell). Because of IR-line overlapping in case of compost air with concentrations of CO_2 above 5 Vol.-%, N_2O above 300 ppm, and saturated water vapor pressure (at ambient temperature) the detection limit for CO deteriorated by a factor of 5 to 10 dependent of compost air composition (Figures 2 and 3). The systematic error in the determination of CO concentrations due to the above interferences was estimated to be less than 20 % for CO concentrations below 1 ppm (20 m cell) and ~10 % for CO above 10 ppm. The error 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 procedure. Errors of the FT-IR-measurements of gas samples, caused by electronic noise, gas handling, and other stochastic sources were estimated to be in the range of 5 %. Furthermore, the additional error due to gas sampling by flux chambers reduces the accuracy in the determination of emission rates.

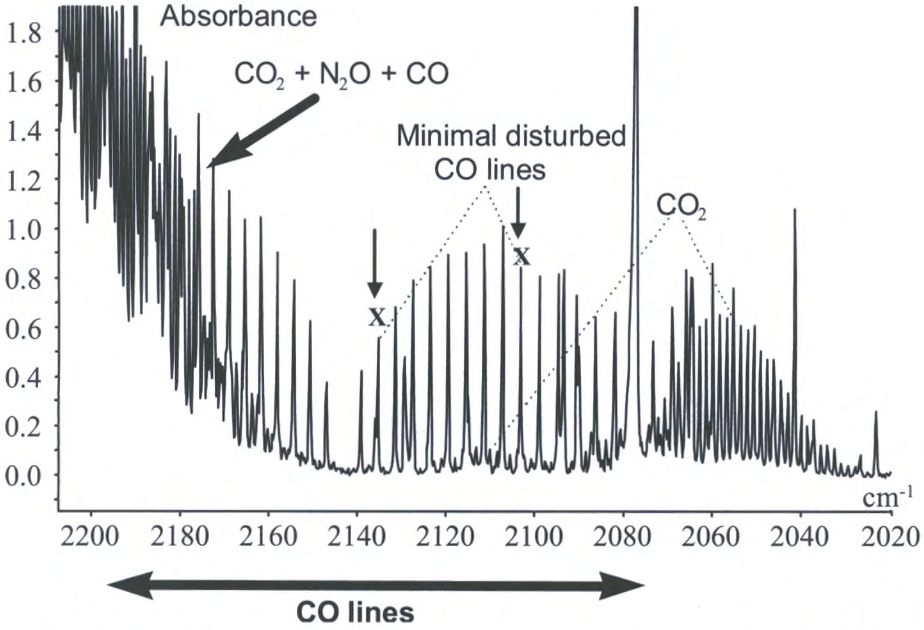

Figure 2. Minimal disturbed FT-IR lines (marked by X in figure) of air from substrate container during laboratory scale composting of hay (mixed herbage) from landscape conservation, 70 % moisture content (w.b.) and amended by calcium ammonium nitrate. Measurement in absorbance mode, resolution 0.2 cm^{-1}, temperature 35 °C, aeration rate 50 cm^3 min^{-1}. CO: 173 ppm; CO_2: 19.1 Vol.-%; CH_4: 1.7 ppm; N_2O: 281 ppm; NH_3: 0.9 ppm.

FT-IR Calibration and Concentration Measurements

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

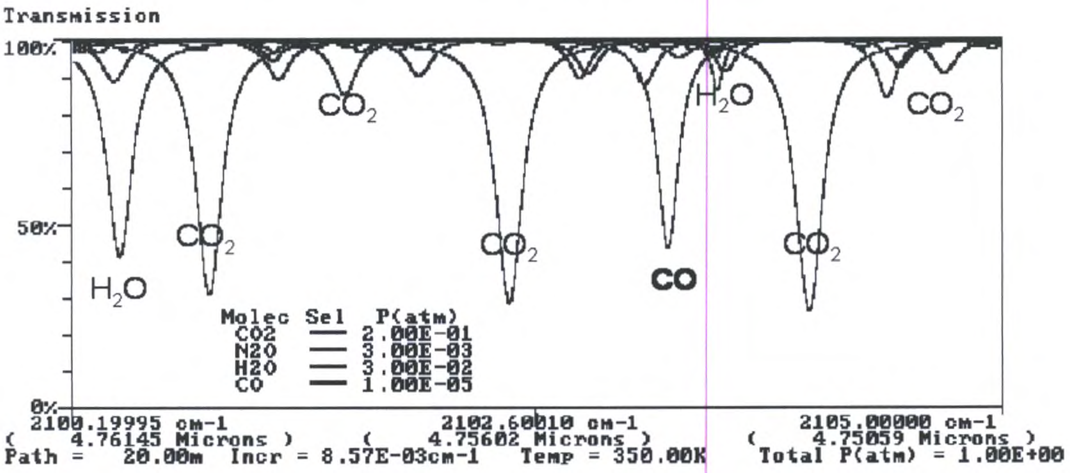

Figure 3. HITRAN simulation of spectral lines between 2100.2 cm^{-1} and 2105.0 cm^{-1} The CO line at 2103.2 cm^{-1} is nearly undisturbed (CO: 10 ppm; CO: 20 Vol.-%; N_2O: 3000 ppm; H_2O: 22 g m^{-3} – 100% humidity at 24°C).

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

CO-Flux Measurements During Laboratory Compost Studies

For laboratory experiments, the plant material (1 kg sun dried mixed herbage from landscape management and conservation) was wetted up to a moisture content of ~70 weight-% by soaking with two liters of water and waiting for 24 h. Composting studies were performed with nitrogen amendments, specific CO studies at a later date without any amendment except water. The wetted plant material was then placed into a temperature-controlled, ventilated chamber applying a constant air exchange rate (Figure 4). Substrate temperature was monitored with thermocouples in the center, top, and bottom of the chamber. Experiments were carried out to study emission rates of different gases as influenced by substrate temperature, moisture content, and nitrogen content, and chamber aeration rate. The latter was manually regulated via a peristaltic pump and viscosity flow meters and the exact rate was measured by a drum gas meter (Ritter®, Figure 4). The composition of the input air and of the air leaving the chamber was analyzed by FT-IR. Gas production rates were calculated on the base of volume flow rates and concentration differences.

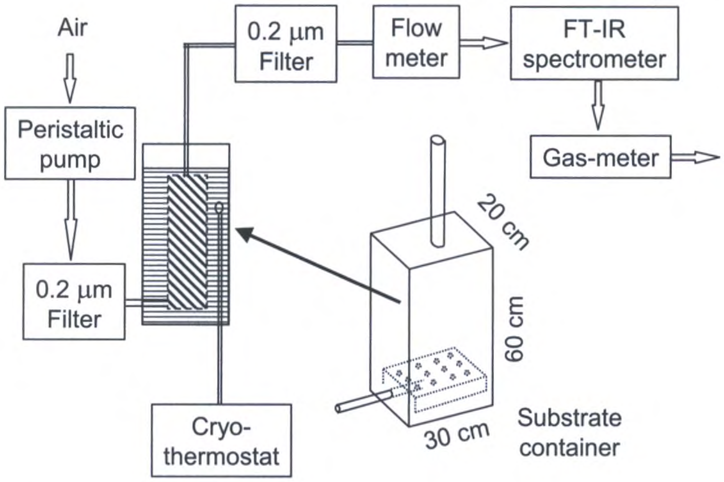

Figure 4. Scheme of laboratory gas measurements.

CO-Flux Estimates at Green Waste Compost Heaps

For the composting of green waste, a typical, trapezoidal compost heap was made of mixed green waste from landscape management and conservation. The initial dimensions of the compost heap were 11 m x 7 m x 3 m high. The initial mass of the compost heap was 14800 kg with a carbon content of 4300 kg. Its mass was measured by means of a trailer and two axle balances with a resolution of 20 kg and an accuracy of 50 kg at maximum load of 25 t. Mass measurements were repeated after heap turnover 32 and 70 days after start and at the end of composting at 194 days. The carbon content of the material was analyzed by means of three mixed samples of the compost material using a TOC analyzer. The initial carbon mass decreased to 730 kg after rotting. For gas sampling, compost air from inside the heap was sampled by a small diaphragm pump through inserted polyethylene pipes at nine different measuring points into gas bags each of 10 dm^3 volume at each measuring day (Figure 5).

CO-Flux Measurements at Dung-Windrows

The CO flux from dung windrows was calculated from concentration increases inside static gas flux measuring chambers, which had had a volume V of 0.189 m^3 and a bottom area A of 0.292 m^2. Preliminary studies using CO_2 sensors with data loggers (Testo AG, Model 950) and a photo-acoustic multi-gas monitor (Brüel & Kjær, Model 1302) indicated that a sampling time of 10 min was sufficient for a flux measurement under most circumstances. (Hellebrand and Kalk, 2000; 2001).

Results and Discussion

CO from Green Waste Compost Heaps, from Dung Windrows, and from Plant Litter

The experimental results indicated that CO production depends on the availability of oxygen. Initially, similar maximum CO concentrations were observed at all measuring tubes after onset and after turnover of the compost heap. After significant progress of the composting process, highest CO concentrations were observed at measuring tubes 1, 4, and 7 in the upper layer of the compost heap, and lowest CO levels were measured at the bottom part of the heap (pipes 3, 6, and 9 in Figure 5), consistent with a typical aeration, i.e. O_2 availability gradient inside a compost heap. The mean of the concentrations measured at the nine tubes was utilized for the determination of the total emissions in connection with weighing and analysis of the rotting compost material. Over the six months of composting, 3570 kg carbon were released as CO_2-C and 1.7 kg as CO-C (approximately 0.04 % referring to the initial carbon mass or around 0.05 % with reference to CO_2-C). In relation to the surface, the mean CO flux was 20 mg CO m^{-2} h^{-1} (Hellebrand, 1998).

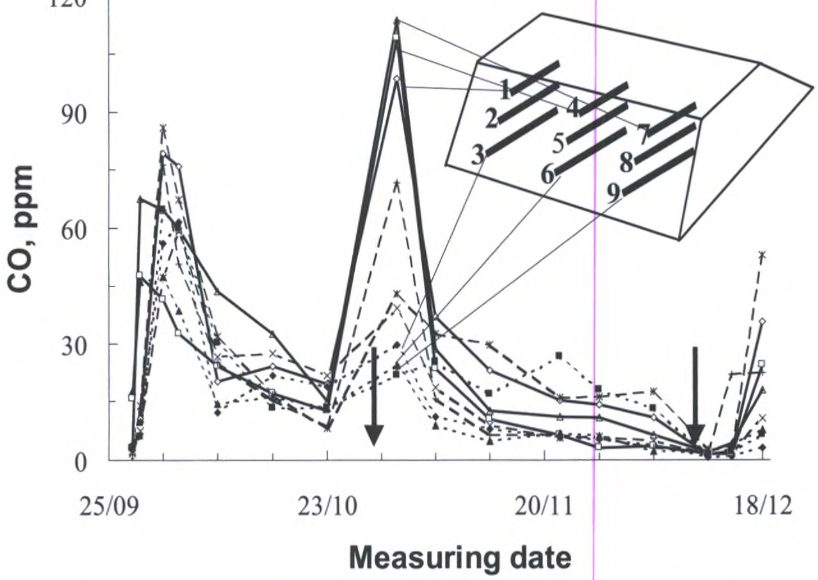

Figure 5. Concentration of CO at the different measuring tubes and scheme of compost heap with measuring tubes (mixed herbage from landscape conservation on bare soil). Arrows indicate dates of turning the compost.

Similar emissions were measured during composting of farm waste. At fresh windrows of animal waste, the flux rates were between 30 and 100 mg CO m^{-2} h^{-1}. After a period of one to two weeks, emissions dropped to very low levels, and during early spring and late fall, uptake was occasionally recorded when the ambient CO mixing ratio was high. The accumulated CO emissions during composting of farm waste were calculated by interval integration. Per composting period, the total fluxes were between 1.6 and 3.7 g m^{-2}. Six periods between seven weeks and up to three months of windrow composting of farm waste were evaluated. The mean emission from all periods was 3 g m^{-2} and a mean value of 4×10^{-4} was calculated for the ratio between total CO-C and CO_2-C fluxes.

Enhanced CO levels were also observed during several test measurements of air sampled from heaps of fallen leaves and heaps of mowed grass in different parks of Potsdam. Air from the center of the heaps was taken via polyethylene pipes and gas bags using a small diaphragm pump. The measured concentrations ranged from 3 to 22 ppm.

CO from Sterilized and Non-Sterilized Hay (Mixed Herbage from Landscape Conservation)

After evidence of CO emissions from composting had been established, the influence of temperature (Figure 6) and aeration rate on emissions was analyzed by laboratory measurements using hay from landscape management and conservation (sun dried mixed herbage). The results were puzzling at first, as they showed an initial maximum of CO after incubation, dropping to a nearly constant but much lower level for about four days, then rising slightly again.

An explanation may lie in the way the experiment was performed, not allowing sufficient aeration (constant rates between 25 and 150 cm^3 min^{-1}) to keep the substrate aerobic while drying it slowly at the same time. If CO-emissions are indeed of thermochemical instead of biochemical origin, the previously established emission dependence on O_2 availability and wetness (Schade, 1997) predicts a higher initial emission when the material is wet and has not consumed the chambers O_2 significantly yet. Emissions then drop because the composting becomes partially anaerobic due to the low aeration rate. As the material dries out, a more aerobic environment is slowly reestablished and CO emissions start increasing again, albeit at lower levels as the material is drier.

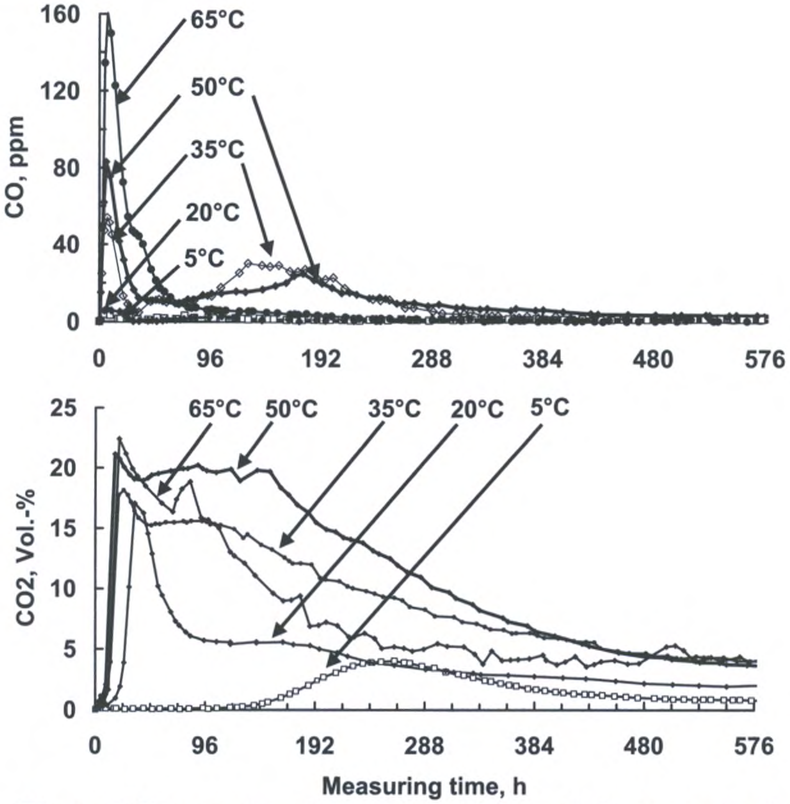

Figure 6. Temperature influence on CO and CO_2 concentration trends in the air from degrading of hay (mixed herbage) from landscape conservation, 70 % moisture content (w.b.), ventilation rate 25 cm^3 min^{-1} kg^{-1} substrate.

To test the thermochemical CO emission assumption, the filled substrate container, separated by bacteria-tight 0.2 μm filters from ambient air, was sterilized in an autoclave at 136 °C for three hours. The subsequent measurements of CO_2 inside the chamber (previously 20 Vol.-% versus now 0.2 Vol.-% (Figure 7)) proved the effectiveness of the sterilization, while, at the same time, nearly unchanged CO levels evidenced thermochemical oxidation as the dominant CO emission process.

The level of CO and CO_2 inside the chamber was dependent on temperature. An Arrhenius plot of calculated formation rates after the minimum (mean values of the periods from 96 h to 144 h) resulted in activation energies of ~65 kJ mol^{-1} (CO) and ~43 kJ mol^{-1} (CO_2) for the samples without sterilization (Figure 8). In experiments with sterilization, the Arrhenius plot of production rates (mean values of the periods from 48 h to 144 h) gave activation energies for the thermochemical oxidation of ~52 kJ mol^{-1} for CO and ~30 kJ mol^{-1} for CO_2 (Figure 9). These findings are in line with the results obtained by Schade (1997; Schade et al., 1999).

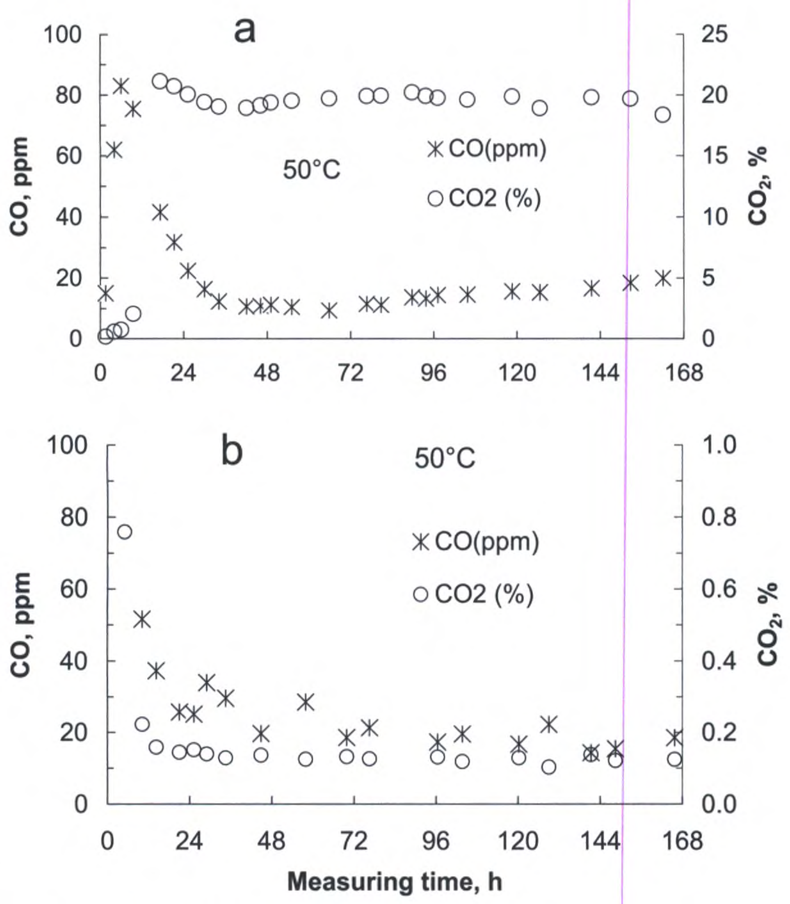

Figure 7. CO and CO_2 concentration trends in the air from degrading of hay (mixed herbage) from landscape conservation, 70 % moisture content (w.b.), temperature 50 °C, ventilation rate 25 cm^3 min^{-1} kg^{-1} substrate.
a) without sterilization b) sterilized for 3 h at 136°C

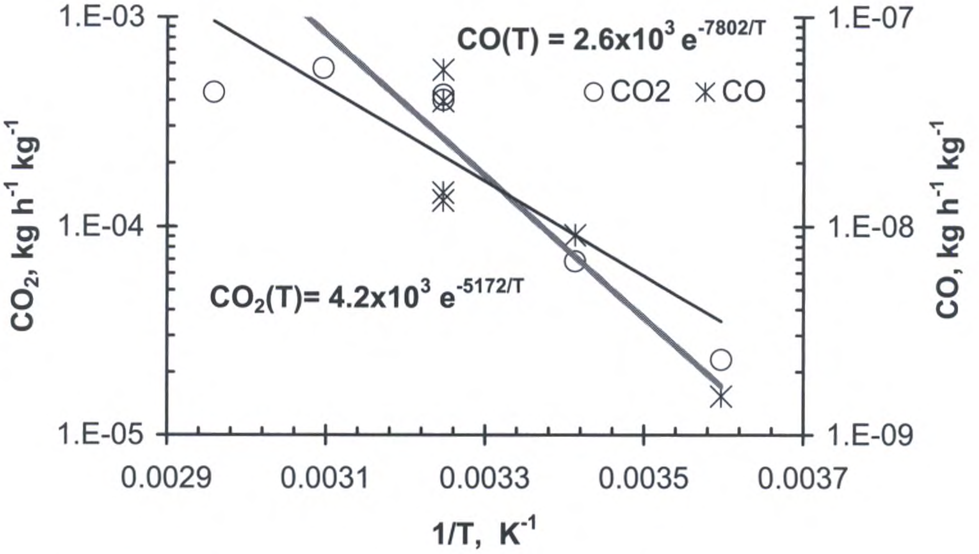

Figure 8. Production rates of CO and CO_2 between 278 K and 338 K plotted against inverse temperature. Non-sterilized substrate, 70 % moisture content (w.b.), ventilation rate 25 cm^3 min^{-1} kg^{-1} substrate.

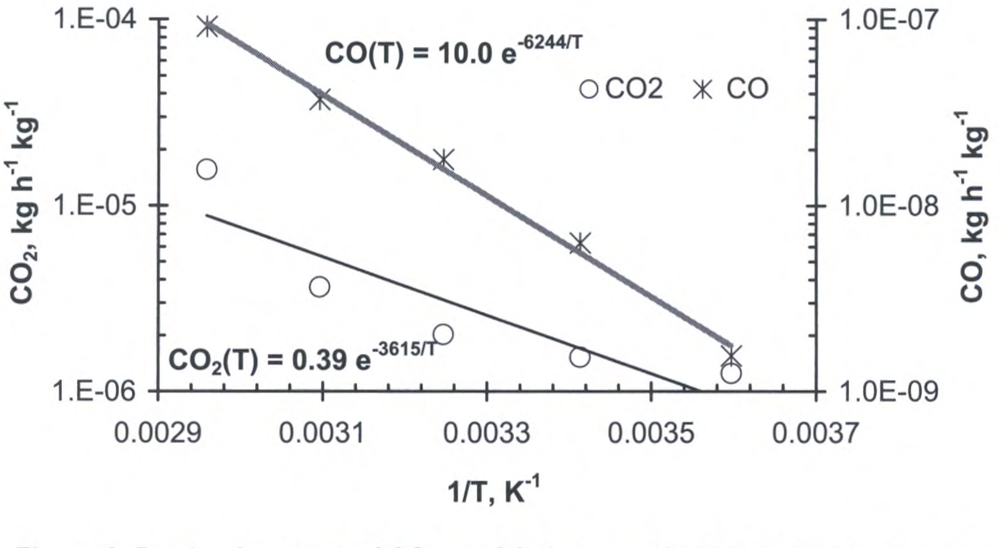

Figure 9. Production rates of CO and CO_2 between 278 K and 338 K plotted against inverse temperature. Sterilized substrate, 70 % moisture content (w.b.), ventilation rate 25 cm^3 min^{-1} kg^{-1} substrate.

Conclusions

Very high concentrations of CO have been observed inside dedicated composting and other heaps of degrading plant matter. Flux chamber measurements confirmed that CO is emitted to the atmosphere from the composting process and its ratio to simultaneously emitted CO_2 lies between 0.1 and 1 ‰ CO-C/CO_2-C. Furthermore, our laboratory measurements confirmed that the production process of CO is independent of microbial activity in the substrate, but is promoted by increased temperatures and wetness, and needs oxygen. These results are consistent with the conclusions of Conrad and Seiler (1985b) and Schade (1997, Schade et al., 1999), and reconfirm that the slow decomposition of organic material is a source of atmospheric CO. The results also confirm that, in principle, CO emissions can be calculated from the activation energy and the pre-exponential factor calculated from Arrhenius plots based on laboratory measurements (Schade and Crutzen, 1999). Previously estimated global CO emissions from this process (~40 Tg CO y^{-1}) were low compared to the dominant anthropogenic sources of CO, such as fossil fuel combustion. However, they may often occur in regions that receive comparatively low inputs of anthropogenic CO emissions, such as in the tropics.

The specific composting processes evaluated here are commonly carried out in Germany for a multitude of organic wastes, including yard wastes and municipally collected household biowastes. Composting facilities in Germany that use the more common aerobic composting process handled an annual throughput of roughly 7200 Gg (1Gg = 1 kiloton) of fresh waste in 2003 (Statistisches Bundesamt, 2005). Based on a wetness of 50% and an assumed average carbon mass loss during the composting process of another 50%, we estimate that between 2 and 20 Gg CO-C may be emitted into the atmosphere from biowaste composting in Germany. That is, compared to dominant road traffic emissions of 1700 Gg CO per year (UBA, 2005), a relative amount of less than 1%, and therefore likely not contributing significantly to tropospheric ozone formation. Although negligible on this basis, CO emissions from the composting facilities may contribute significantly to local air pollution under stagnant meteorological conditions.

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Comparing Field Odor Assessment Methods with an Atmospheric Dispersion Model for Calibrating Setback Estimation Tools for Livestock

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Abstract

Downwind odor assessment to develop setback estimation or siting tools for new livestock facilities is a high priority in several states. The University of Nebraska is currently developing an Odor Footprint Tool (OFT) to assist livestock producers and the general public in understanding the impact that odors have on downwind residents. Air dispersion modeling is a promising approach for assessing the area near livestock facilities for odors. A Gaussian plume dispersion model, AERMOD (AMS/EPA Regulatory Model) was used to predict downwind concentrations for the OFT. Calibration of this procedure was conducted by human receptors using two different methods, on-site intensity and mask scentometry. There was only a weak relationship between mask scentometry and field intensity (R^2=0.51). The experiments were conducted at cattle feedlots and swine lagoons. Several statistical tests were used for assessing model performance, it appears that the mask scentometer technique agrees better with model predictions than field intensity. Field techniques to ground truth models are needed to better understand and predict odor impact to communities.

Introduction to Field Odor Assessment

Field olfactometry is defined as the use of a technique or device to determine dilutions to threshold (D/T) of an odor in the ambient atmosphere. The individuals making such measurements have been referred to by a number of names, including nasal rangers, field sniffers, (field) odor assessors, and (field) odor surveyors. Scentometers were first developed in the late 1970's by Barneby and Sutcliffe and are a low-cost (about $500 per unit) portable instrument (Sheffield, 2004). The scentometer dilutes ambient air with air that has been "cleaned" by a charcoal chamber. Disadvantages of the instrument include a lack of control of inhalation rates by different panelists, the discomfort of glass inhalation tubes, the odor fatigue caused by poor nasal sealing to the glass ports, and the inability to prevent olfactometry fatigue between measurements.

The mask scentometer (Henry, 2004; Sheffield et al., 2004), as shown in Figure 1, is functionally similar to a conventional box scentometer. It is comprised of a ¼-face respirator mask with two cartridges. The first cartridge is fitted with a charcoal filter having a plenum and two ¼-inch holes for drawing air into the mask. The second cartridge is fitted with a dial mechanism that is rotated to change the ratio of filtered air to ambient (odorous) air to established dilution ratios of 170, 31, 15, 7, and 2. The advantage of the mask scentometer is that it minimizes odor fatigue, allows for one-handed operation, and can be easily operated over long periods of time without fatigue. Users sniff the air that is drawn through the two sets of ports and mixed within the mask chamber, generally going from the highest dilution setting to lower dilution ratios in order to determine the dilutions to threshold. Users adjust the dial setting every 5-8 seconds, allowing a D/T measurement to be taken every 30 seconds.

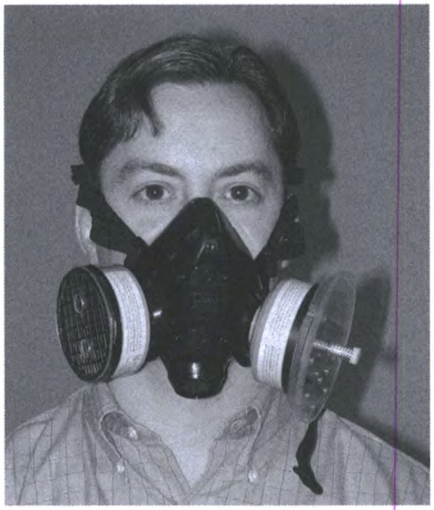

Figure 1. Mask Scentometer

The field intensity method was developed by the University of Minnesota, adapted from ASTM Standard E 544-99 "Standard Practices for Referencing Suprathreshold Odor Intensity." The method references field intensity measurements to a standardized n-butanol scale. The scale used was adapted from the static scale method of 12 concentrations ranging from 10 to 10,000 ppm n-butanol, reduced to 5 levels so that the odor intensities can be committed to memory by assessors. When measurements are made in the field, assessors wear a ¼-face respirator mask between intensity assessments. In the typical scenario, 60 intensity assessments can be made in 10-15 minutes.

Sheffield et al. (2004) conducted a 6-week study of five odorous sources in Idaho to quantify the variability of field and laboratory olfactometry methods and their correlation to odor intensity, as well as ammonia and hydrogen sulfide concentrations. The comparison of four olfactometers indicated that the use of laboratory olfactometry (dynamic, triangular forced-choice) or Nasal Ranger® field olfactometers resulted in the least amount of variability across odor sources. Significant differences with poor correlation were found between odor intensity methods and the use of Tedlar bags for storage of ambient air samples.

The University of Minnesota employed trained panelists as field sniffers and using the field intensity data they collected to scale INPUFF-2 model results in the development of the Odor From Feedlots Setback Estimation Tool (OFFSET). The procedure implemented was a modified version of the one used in Germany by Hartung and Jungbluth (1997). Seven individuals were deployed perpendicular to a centerline marked off from 25 to 400 meters from the source and spaced 5 to 20 meters apart. They were provided with stopwatches, charcoal filter masks, and clipboards with data sheets. Field intensity measurements were assessed once every 10 seconds for a 10-minute period. The masks were removed only long enough (a few seconds) to assess the intensity of the ambient odor (Jacobson, 2000).

Since the early 1980s air dispersion models have been studied to predict odor concentrations downwind from livestock sources (Janni, 1982; Caeney and Dodd, 1989; Mejer and Krause, 1985; Lorimer, 1986; Omerod, 1991; McPhail, 1991; Gassman, 1993; Chen et al., 1998). Only a few studies exist comparing the results of dispersion models to field odor panelists (Li et al. 1994; Hartung and Jungbluth, 1997, Zhu et al., 2000; Guo et al., 2001).

Methodology

Assessments were made at a manure treatment lagoon from and two cattle feedlots. Sites were selected that were topographically level surrounding the source, were isolated from other odor sources, and had few or no obstructions surrounding the site within 500 meters. This was deemed to be most desirable for dispersion modeling and to minimize unwanted odors from other sources.

The data set represents downwind odor data from a lagoon assessed on two different days - once in the fall of 2003 and once in the spring of 2004 - and two different feedlots one assessed in the spring of 2004 and the other in the fall of 2003. At least 7 and up to 10 individuals were used to form transects downwind of the facility on the days of the experiments.

Lagoon

The lagoon treated manure from 1,250 swine finishers, 800 sows and gilts, and 800 nursery pigs. The anaerobic lagoon was typical of many Nebraska lagoons and was uniquely situated 1/2 mile to the east of the production barns. This allowed the researchers to isolate the lagoon odors from other odors from the facility or neighboring odor sources. The lagoon was situated just south of an east-west gravel road, and was surrounded by cropland with little topographical relief surrounding the facility in all directions.

The flat terrain allowed transects to be set up to the north of the facility on a fall day when the prevailing wind was from the southwest. Transects were established at 111, 153, 198, and 246 meters from the lagoon. The day of the assessment was warm and sunny, with no cloud cover and a very gentle and shifting breeze. Wind speeds during these assessments were between 1-3 m/s (A and B stability class).

On the day of the spring assessments, the wind was from the northeast instead of the south. Transects were established downwind at 58, 73, 103, and 134 meters. Atmospheric conditions during the day would be described as sunny with 4-7 m/s wind speeds (A and B stability class).

Feedlot

The capacities of the studied feedlots were 4,200-head and 1,600 head, and both were located in central Nebraska. Terrain near the facility had very little topographical relief. The width of the source was several times greater than the width of the sniffer transect. Odor monitoring was conducted on a warm, sunny and windy spring day and a cold overcast day. Wind speeds during the warm assessments were between 3-5 m/s (and B and C stability) and 5-9m/s (and D stability class) for the colder assessments. Transects were established downwind at 150, 265, 390, and 504 meters for the warmer feedlot assessments and at 106, 308, and 505 meters for the colder feedlot assessments.

Assessment Technique

Individuals, or field sniffers, were recruited who could refrain from drinking caffeinated drinks, eating spicy foods, and wearing perfume and cologne on the days of participating in the study. Field sniffers attended a daylong training seminar that instructed them in the use of the mask scentometer and how to assess odor intensities. Mask scentometer readings or "Mask DT's" are taken by turning a dial on the mask through a series of notches that correspond to increasing dilution ratios of ambient air (odorous air) to air that has been cleaned with a carbon filter (clean air) (Henry, 2004). When the dilution first reaches the point at which the sniffer can recognize the odor, this DT is recorded. This DT is considered to be the same as an Odor Unit (OU), which can be used directly for model comparison.

Next, sniffers recorded odor intensities. Sniffers were trained to correlate livestock odors with a reference odorant, n-butanol. Sniffers used the Minnesota 10- step n-butanol scale ranging from 0 to 5 in ½-step increments, where 1 is considered barely noticeable and 5 is considered very annoying. Sniffers removed their masks briefly to take this measurement between breaths. Odor intensity was then converted to D/T and compared to model predictions for use in scaling and calibrating models.

Experimental Set-up

A weather station was placed on the facility the day before a sniffing event by a researcher. It was located, if possible, in the plume where the sniffers were expected to locate the next day. The weather station was instrumented to record, net solar radiation, temperature, relative humidity, wind speed, wind direction, solar heat flux, and barometric pressure.

On the day of the experiment, sniffers calibrated them selves at a location away from the plume near the site with n-butanol. They also calibrated themselves against each other, by subjecting themselves to varying levels of the target odor (near outer fringes of plume) and agreeing among themselves that they were all reporting intensity and scentometer readings consistently. They would dawn their masks before entering the plume. First, mask scentometer measurements were taken every 30 seconds, evaluating every DT within the range of the instrument, if no odor was detected, a 0 was recorded. Mask scentometer measurements were taken for 15 minutes. Next, field intensity measurements were taken every 15 seconds for 15 minutes. The sniffers were instructed to become familiar with the target odor and make their assessment on the target odor, this was done to minimize the influence of background odors that at low concentrations can produce a false positive. Sniffers collected intensity data every 15 seconds for 15 minutes, and dilution to threshold (DT) from a mask scentometer every 30 seconds for 15 minutes. Each sniffer was stationed at a location in the transect for a 30 minute period before moving to another location. Sniffers were randomly located in each transect, and no sniffer was ever in the same position in the transect on the same day. The mask allowed sniffers to collect two odor measurements sequentially. After a sniffer was notified to start taking measurements, they began taking mask scentometer assessments. After they finished, they waited for the odor intensity signal start, and then collected odor intensity measurements. When they finished with these they would move on to the next transect.

Sniffers recorded measurements on a data sheet. Stopwatches were used that could be set to chime at a set interval. A lead sniffer was identified and synchronized his watch with the weather station clock so measurements would correspond to modeled data. The lead sniffer would then start all of the sniffers at the same time. Sniffer responses were arithmetically averaged for each assessment, therefore the average for a assessment represents the average of 30 measurements for the mask scentometer and 60 measurements for field intensity. In total there were over 4,500 mask scentometer assessments and 9,000 field intensity assessments conducted over the course of the study.

Emissions

All sites studied were area sources and measured using a stainless steel wind tunnel device. The tunnel, shown in Figures 2 and 3 was constructed according to plans from Schmidt and Bicudo (2002) originally designed by Jiang et.al. (1995), consisting of an inlet PVC stack, blower, expansion chamber, air filter, pressure gauge, tunnel body, mixing chamber, outlet PVC "T" and two gas sampling ports. Wind tunnels are portable, open-bottomed enclosures that are placed over the emitting surface. Ambient or filtered air is drawn or blown through the tunnel to mix with and transport the emissions away from the emitting surface. This is intended to simulate the convective mixing and transport process present above the emitting surface.

Figure 2. Collecting Emissions with a wind tunnel from a lagoon

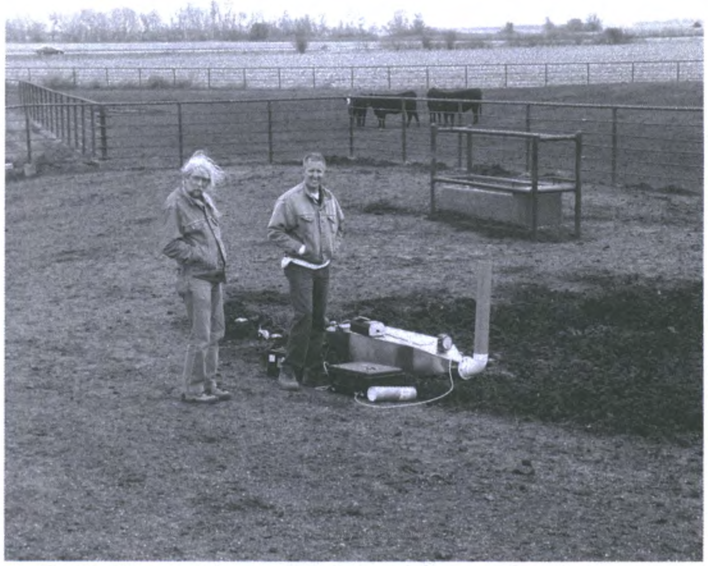

Figure 3. Collecting Emissions with a wind tunnel from a feedlot

Emissions were estimated by collecting a bag sample and having that sample analyzed by an olfactometry lab. The reported dilution to threshold was then converted to a standard emission rate adjusted for height and wind speed of 1 meter height and 1 meter per second. The emission rates were then adjusted for each model run for varying wind speed and stability class. It is accepted that atmospheric stability effects odor emission rate. This is because stability affects both the slope of the wind speed profile and the degree of turbulence. Odor concentrations measured using wind tunnels were adjusted to a standard 1m/s and 1 meter high standard emission rate (Table 1), using a procedure outlined in Smith and Watts (1994).

Hence, for the wind tunnel data, the odor emission rate varies with tunnel wind speed according to:

$$EV = EM * (u_T/u_M)^{0.63}$$

Where,
EV = Odour emission rate at tunnel wind speed, u_t
EM = Base odour emission rate measured at tunnel wind speed, u_m
u_T = wind tunnel speed (m/s)
u_M = Tunnel wind speed for measurements, i.e. 0.3 m/s.
0.63 = adopted exponent (for feedlots), 0.5 for lagoons

The formula to convert wind speed at 10 m (for example) to wind speed at 0.125 m (i.e. tunnel speed) in neutral stability is:

$$U_T = U_{10} * LN\ (0.125/Z_{0-2})/\ LN(10/Z_{0-1})$$

Where,
U_t = wind tunnel speed (m/s) at 0.125 m
U_{10} = wind speed (m/s) at 10 m
Z_{0-1} = surface roughness for anemometer at 10 m (0.3 m)
Z_{0-2} = surface roughness for pond (0.03 m).

Kaye and Jiang (1999) outline a procedure (Table 1) to adjust emissions for use in AUSPLUME for stability and wind speed. The procedure is theoretical and not substantiated with experimental data, but is reasonably consistent with Ormerod (1991 and 1994).

Table 1. Adjustments made to emission rates based on wind speed and stability class (Kayle and Jiang(1999)

Wind Speed Category	Speed Rate (m/s)	Median Wind Speed (m/s)	Stability Class A	B	C	D	E	F
			Relative Odour Emission Rate (%)					
1	0-0.6	0.3	86%	86%	80%	72%	46%	30%
2	0.6-1.2	0.9	149%	149%	139%	125%	80%	52%
3	1.2-1.8	1.5	192%	192%	180%	161%	104%	67%
4	1.8-2.4	2.1	227%	227%	213%	190%	123%	79%
5	2.4-3.0	2.7	257%	257%	241%	216%	139%	90%
6	>3.0	6.5	399%	399%	374%	335%	216%	139%

Emissions collection from area sources such as lagoons and feedlot surfaces are difficult to perform. In this study, the samples were in the lower ranges of detection capable by the laboratories used and were in the range of 8-34 DT. Another issue with respect to the olfactometry results is the lower detection limit (LDL) of the olfactometer. The LDL is the lowest value of the air quality characteristic which can be distinguished from a zero sample. Most olfactometers have a detection rate of 20-50 OU/m3 (Gostelow et al., 1993). Given that some of the olfactometry results used to determine emission rates are below the LDL of the olfactometers, there is a large degree of uncertainty concerning the emission rates of the sources studied. The emission rates used for each of the assessments is shown in Table 2.

Table 2. Emissions used for Individual Model Runs

Location	Run	Time	Emission OU/m^2s	Stability class	Wind speed m/s
Lagoon 1					
	1	Met tower failure			
	2	1:50-2:20	4.7	B	2.7
	3	2:30-3:02	3.5	B	1.5
	4	3:09-3:40	2.7	A	0.9
Lagoon 2					
	1(DT)	10:05-10:39	8.9	B	5.4
	1(I)	10:05-10:39	8.8	A	5.2
	2(DT)	11:27-12:00	9.8	B	6.5
	2(I)	11:27-12:00	9.4	B	6.1
	3(DT)	10:47-11:20	9.7	B	6.4
	3 (I)	10:47-11:20	9.1	B	5.6
	4(DT)	10:05-10:39	7.0	A	3.3
	4(I)	11:13-11:39	8.2	B	4.6
	Random	14:47-15:03	8.4	B	4.8
Feedlot 1					
	1	9:53-10:35	15.1	D	8.6
	2	11:16-11:47	14.8	D	8.3
	3	12:05-12:30	13.6	D	7.3
	4	2:00-2:31	12.3	D	6.2
	5	2:49-3:19	12.6	D	6.4
	6	3:32-5:02	11.2	D	5.3
Feedlot 2					
	1	10:57-11:27	2.3	C	3.2
	2	11:41-12:11	2.7	C	4.4
	3	12:14-12:50	3.0	C	4.9
	4	13:02-13:38	2.8	C	4.4

Modeling

The adjusted emission rates were then used to model each individual assessment session. The source or sources were created in AERMOD as area sources. On-site meteorological data was collected at 1-minute time steps, and applied to the model. AERMOD and most models only accept 1 hour time step meteorological data, so 1-minute time step data was modeled as hourly data and assumed to be 1-minute predictions without any adjustment.

Relationship Between Field Intensity and Mask Scentometer

The first analysis completed was to determine if a relationship existed between the field intensity method and mask scentometry (Mask DT). It was assumed originally that only one method would be needed to develop the scaling factors for the dispersion model, but if both methods produced the same result, then one could be abandoned for the superior method.

Field data from assessments was processed for each assessment event. Each time a sniffer collected data over the 15 minute period the data was averaged and a maximum and minimum value was determined. It is assumed that the odors were similar in magnitude during the 15-minute assessment period, and the on-site meteorological data was queried to determine if wind speed and direction would have changed substantially to invalidate this assumption. All measurements were taken during consistent conditions and were in the A-B atmospheric stability classes as defined by the SRDT method (USEPA, 2000). It is assumed that the odors during the assessment period were relatively consistent and back-to back measurements can be compared . Individual responses were converted to the actual DT observed, and the individual intensity responses were converted to DT as per Jacobsen et al (2000). The results reflect the average of the DT's for an assessment period. It should be noted that taking the average of the intensities converted to DT will yield a different arithmetic result. The equation for converting swine intensities to DT is shown below:

$$DT_{swine} = 9.429\left(e^{1.085I}\right)$$
$$DT_{beef} = 8.367\left(e^{1.078I}\right)$$

Where I is the intensity of the odor as determined by a trained assessor.

The conversion for the mask scentometer was also done according to Table 3.

Table 3. Mask Scentometer Settings

Dial Position	Mask Scentometer D/T
1	170
2	31
3	15
4	7
5	2

The calculated field intensity DT and mask scentometer (mask DT) by the same sniffer at a given location downwind of the source emission were compared. A statistics analysis was completed and the results are shown in Table 4. As can be seen, the mean of the mask DT is almost an order of magnitude less than the mean response from the field intensity or field DT.

Table 4. General Statistics of Mask DT and Field Intensity DT

Mask Scentometer DT		Calculated Field Intensity DT	
Mean	5.1	Mean	58.2
Standard Error	0.97	Standard Error	8.0
Median	1.8	Median	17.9
Mode	0.1	Mode	14.3
Standard Deviation	9.0	Standard Deviation	73.5
Sample Variance	80.7	Sample Variance	5,395.8
Kurtosis	16.9	Kurtosis	5.1
Skewness	3.7	Skewness	2.1
Range	56.8	Range	391.1
Minimum	0	Minimum	8.4
Maximum	56.8	Maximum	399.4
Sum	434	Sum	4,944
Count	85	Count	85
Confidence Level (95.0%)	1.9	Confidence Level (95.0%)	15.8

The standard deviation and sample variance are much less with the mask DT, suggesting that there is less variability with this method than the field intensity method. The mean suggests that the Mask DT is approximately an order of magnitude less than calculated field intensity, which has some implications for modeling because typically model results have been factored up to match intensity assessments by field sniffers (Koppolu et al., 2004).

Next the dataset was analyzed using a t-test assuming unequal variances. The results of a t-test using Microsoft EXCEL are shown in Table 5. The P critical two tail is less than 0.01 indicating that a significant difference between Mask DT and calculated Field Intensity DT. A single factor ANOVA produced the same result.

Table 5. Statistical t-test Results, Mask and Field Intensity DT's

	Mask DT	Field Intensity DT
Mean	5.10	58.17
Variance	80.72	5,395.83
Observations	85	85
Hypothesized Mean Difference	0	
Degrees of freedom	87	
t Stat	(6.61)	
P(T<=t) one-tail	1.47E-09	
t Critical one-tail	1.66	
P(T<=t) two-tail	2.95E-09	
t Critical two-tail	1.99	

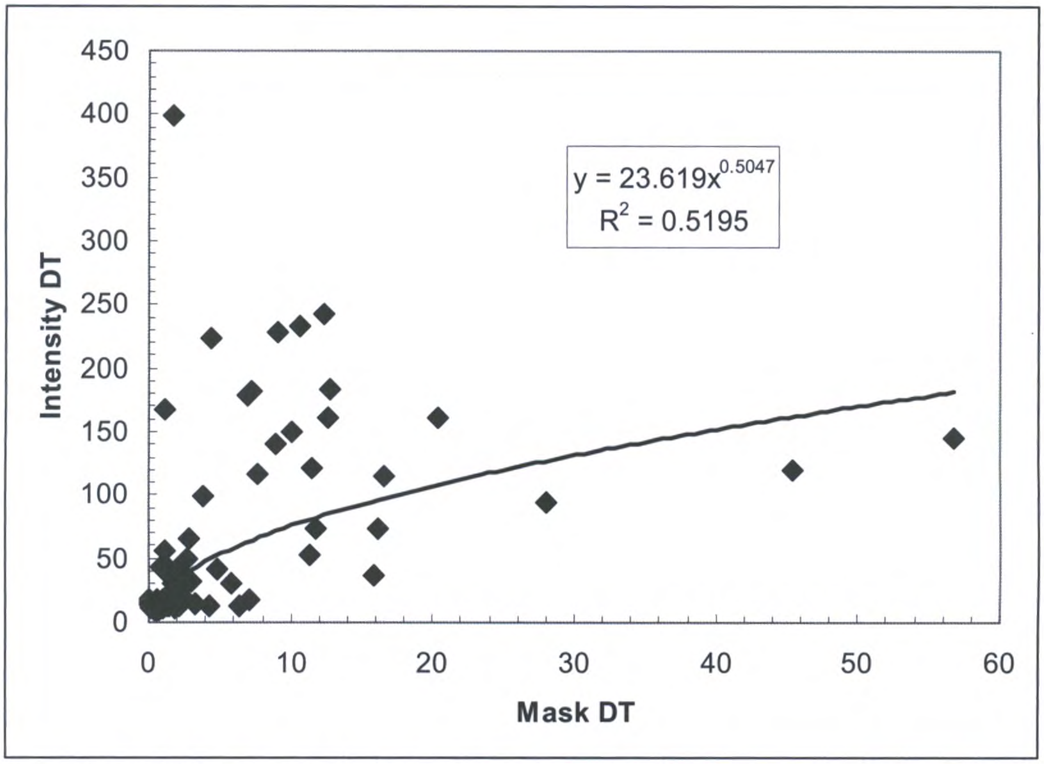

Figure 4. Field Intensity DT versus Mask DT

Figure 4 shows a scatter plot of the calculated Field Intensity DT versus Mask DT. The relationship between the two is best represented with a power relationship and produces a coefficient of correlation of 0.52 (R^2) indicating that there is not a very good relationship between the two methods. A more robust analysis of the relationship between mask scentometry and field intensity is presented in Henry (2005).

Henry (2005) also reported that a relationship between peak and mean measurements may exist for the mask scentometer (R^2=0.75), but that this did not hold true for field intensity (R^2=0.33). Although peak to mean ratio's appeared to be similar for both field methods, scatter for field intensity was more severe than for Mask DT. Finally, Henry (2005) reported that an analysis of individual data revealed that some sniffers provide a consistent peak to mean ratio, while others do not. Additionally some individuals may be very consistent when using the mask scentometer, but not when reporting field intensity, and vice versa. Some were good at both and some at neither. Henry (2005) suggested that that individual sniffer sensitivity be assessed in future work with field assessors and that a similar type of analysis be performed between assessors to ensure consistent results are being reported in any future work that will be used to ground-truth air dispersion models.

Comparison of Model Results to Field Assessments using Statistical Tests

Statistical tests were used to evaluate model performance. In this study, these included model bias, fractional bias, normalized mean square error, root mean square error, skill_v and skill_r by Wilmott (1981), Pielke (1984) and Hurley (2000). Common measures of ascertaining model performance include the mean, standard deviation, coefficient of correlation, and the coefficient of variation as statistical measures.

Model Bias (MB):

$$MB = \frac{1}{n}\sum_{i=1}^{n}(O_i - P_i)$$

Where: Ideal value for MB = zero

N = Number of observations
O_i = Observed
P_i = Predicted

Fraction Bias (FB):

$$FB = 2\frac{\overline{O} - \overline{P}}{\overline{O} + \overline{P}}$$

Where: Ideal value for FB is between ± 0.67; ± 2 *is good*

$\overline{O}$ = Mean of observed values
$\overline{P}$ = Mean of predicted values

Normalised-Mean-Square Error (NMSE):

$$\mathrm{NMSE} = \frac{\overline{O_i - P_i)^2}}{\overline{O}\,\overline{P}}$$

Where: Ideal value for NMSE = zero

O_i = Observed
P_i = Predicted
$\overline{O}$ = Mean of observed values
$\overline{P}$ = Mean of predicted values

Root-Mean-Square Error (RMSE)

$$RSME = \frac{1}{n}\left[\sum_{i=1}^{n}(O_i - P_i)^2\right]^{1/2}$$

Where: Ideal value for RMSE = zero

N = Number of observations
O_i = Observed
P_i = Predicted

Skill_r

$$\mathrm{Skill\_r} = \frac{\sqrt{\frac{1}{n}\sum_{i=1}^{n}(P_i - O_i)^2}}{O_{std}}$$

Where: Ideal value for Skill_r <1

N = Number of observations
O_i = Observed
P_i = Predicted
O_{std} = Standard deviation of observed values

Skill_v:

$$\mathrm{Skill\_v} = \frac{P_{std}}{O_{std}}$$

Where: Ideal value for Skill_v = 1

N = Number of observations
O_i = Observed
P_i = Predicted
O_{std} = Standard deviation of observed values

Table 8 shows the results of the aforementioned statistical tests. While good agreement for all tests is well beyond the range for ideal, with the exception of Fractional Bias, in most cases the mask method is closer to ideal than the intensity method. This suggests better agreement may be expected from model predictions when compared to mask scentometer assessments (and related devices) than field intensity. It should be noted that there is a considerable amount of variability with respect to individual assessors and the oflactometry used to determine the emission rates of the sources.

Table 8. Statistics for comparison of model predictions to Mask Scentometer and Field Intensity Assessments

Test	Ideal	Lagoon 1		Lagoon 2		Feedlot 1AM		Feedlot 1PM		Feedlot 2	
		Mask	Intensity	Mask	Intensity	Mask	Intensity	Mask	Intensity	Mask	Intensity
Model Bias	0	-1.8	11.7	5.2	105	31	86	4.1	52	4.6	32
Fractional Bias	±0.67 to ±2	-1.6	1.5	0.9	1.9	1.4	1.8	0.7	1.8	1.6	1.9
Normalized Mean Square Error	0	10.8	22.7	2.6	59	15.1	34	6.6	38	69	133
Root Mean Square Error	0	0.5	5.5	1.5	25	11	24	2.7	15	2.3	8.3
Skill_r	1	8.7	0.9	1.3	1.5	1.1	1.3	1.0	1.2	1.1	1.4
Skill_v	1	6.5	0.07	0.2	0.01	0.06	0.03	0.08	0.03	0.03	0.01

Comparison of Model Results to Field Assessments using Scaling Factors

For the development of separation distance tools, the scaling factor or peak to mean ratio, is used to "factor" the emission rate of the source for separation distance tools, such as OFFSET (Odor From Feedlot Setback Estimation Tool) and the OFT (Odor Footprint Tool). Measured assessments (both field intensity and mask) were compared to predicted ambient odor levels from AERMOD. These comparisons involve calculating scaling factors (peak to mean ratios) to adjust relatively short-time interval (seconds) odor intensity measurements in the odor plume to AERMOD predictions which are based on relatively long time period (hourly) averages. Depending on the source type (point, area, volume) and the type of facility being modeled Koppolu (2002) reported results indicated that scaling factors in the range of 0.2 to 3900 may be needed to adjust AERMOD predictions to short-term odor measurements.

Scaling factors or peak to mean ratios, a more thorough discussion of the assumptions behind peak to mean ratios is presented in Koppolu (2002), but for the purposes of this paper they are used synonymously. Tables 6 shows the scaling factors for every experiment, each experiment included 3-4 cross sections at distances listed previously. Table 7 show the scaling factors for the different area source types, lagoons and feedlots. Such scaling factors are useful in determining appropriate emission values for OFFSET and the OFT. In general, scaling factors for the mask scentometer are less than those for the field intensity method.

Table 6. Scaling Factors (Peak to Mean Ratios)

	Lagoon 1		Lagoon 2		Feedlot 1AM		Feedlot 1PM		Feedlot 2	
	Mask	Intensity	Mask	Intensity	Mask	Intensity	Mask	Intensity	Mask	Intensity
Average Scaling Factor	0.2	3627	3.3	47.4	6.0	18.2	2.2	18.3	88	136
Standard Deviation of Scaling Factor	0.2	16,525	2.9	55.6	10.0	16.5	4.4	12.6	354	244

	Swine Lagoons		Cattle Feedlots	
	Mask	Intensity	Mask	Intensity
Suggested Scaling Factors	1.8	1837	32	58

Conclusions

Trained field sniffers evaluated ambient odor levels using a mask scentometer and calculated field intensity downwind from a cattle feedlot and swine lagoon. There was a significant difference observed between the method of assessing ambient odors downwind from livestock facilities using a mask scentometer and a field intensity assessment method adapted from the ASTM Standard E-544-99 "Standard Practices for Referencing Suprathreshold Odor Intensity" by the University of Minnesota. It appears that the use of a mask scentometer returns a result an order of magnitude less than the same person who performs a field intensity assessment when done in the field back-to-back. The standard deviation and sample variance of the dataset suggests that there is less variability in the mask scentometer data than the calculated field intensity method.

Scaling factors were determined for two area sources, lagoons and feedlots. Mask scentometer scaling factors for anaerobic lagoons (not to include manure storages) and feedlots were 1.8, and 32 respectively. Field intensity scaling factors for anaerobic lagoons were found to be 1,837 and 58 respectfully. The smaller scaling factors indicate a closer agreement to model predictions. Several statistical tests were used to evaluate the agreement between the field methods and model predictions. While none of the tests, except fractional bias, reported ideal results, mask scentometer and AERMOD predicted results were in general closer to ideal values than field intensity assessments. This suggests that the mask scentometer, and similar devices operated in the same fashion and with a similar technique (many consecutive measurements over a given period of time) has better agreement with model predictions. This research suggests that AERMOD odor predictions are in better agreement to mask scentometer assessments than field intensity assessments. This finding has substantial implications to the ground-truthing of atmospheric dispersion models.

Acknowledgements

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A Novel Concept for Modeling Odor Impact from Feedlots

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Abstract

Emissions from feedlot operations are known to vary by environmental conditions. Estimating the emissions from feedlot sources for modeling odors is a difficult challenge. A new approach using a feedlot hydrology model to derive necessary inputs for a feedlot emissions model has been developed. A feedlot pad emissions model that predicts emissions as a function of pad temperature, pad depth, and pad moisture content has been developed. A second model that predicts the emissions from sediment basins and holding ponds and is a function of days since rain, inflow volume, inflow ratio (pond volume), and temperature has been developed. Additionally, appropriate emission values for manure and compost storage areas have been investigated. The use of a feedlot hydrology model to estimate the variables for use in the emissions model allows for variable emissions for existing or proposed sites to be predicted over a long time horizon. The application of this process can be used to model odor impact from feedlots with atmospheric dispersion models. Such an application allows for variable emissions based on climate changes, management, and site-specific conditions. A possible application of this process is the development of simple separation distance tools for small to medium sized feedlots. The feedlot emissions predictions used in the model were based on an extensive set of odor samples collected by a wind tunnel over a range of environmental conditions. A brief explanation of the methodology is presented.

Introduction

Determining appropriate separations between livestock facilities and communities and residences has been an intensely studied issue for two decades in Australia. Estimating the odor emissions from animal production facilities is not an exact science. Most separation distance guidelines, setback tools, or odor criteria have been established using empirical formulae or average annual emissions with wind tunnels or flux hoods and dispersion models. Under dry conditions, well managed feedlots can be characterized by low odor emitting sources per unit area, but with vast size comparatively. Feedlot odor emissions under wet conditions may be 1-2 orders of magnitude higher. Feedlot sources are inheritably difficult to collect emissions from because of the low odor concentrations experienced, and the complex range of factors influencing emissions. Finally, other production area sources such as manure storage areas, compost piles, holding ponds, and sediment basins have generally not been previously considered as sources in the modeling of odors from feedlots.

Background

Emissions from feedlots can be separated into several different sources, each with their own characteristics and with variables that define their emission characteristics. The major odor sources at feedlots determined in this study include:

- Feedlot pad or surface emissions: The production area where the cattle are fed. The feedlot pad will have the largest area, will be increasing in pad thickness slowly, followed by a rapid decrease as cleaning occurs. Pad emissions will be most influenced by temperature, depth of manure, and moisture content.
- Sediment basins: Sediment basins are used to collect runoff from the feedlot production areas, temporarily hold runoff from rain events and slowly release them to holding ponds. Sediment basins are characterized as being wet and full of solid laden liquids for several days after a runoff event, and being dry the rest of the time. Sediment basin emissions are influenced by inflow/volume ratios, days since rain, and temperature.

- Holding ponds: Holding ponds are permanent, usually lined structures that store runoff water until it is appropriate to land apply the effluent to cropland. Typically they have a wetted surface year round, unless they are pumped dry. Traditionally they are allowed to fill to their capacity and pumped to their lowest level. Holding ponds emissions are influenced by inflow/volume ratios, days since rain, and temperature.
- Manure storage areas: These are area where manure from the feedlot surface or pad is collected and stored until land application. These areas are characterized by being open areas of piled manure. Manure pad emissions are relatively stable, but are influenced by disturbance to the crusting layer, if present.

The primary odor emission source from feedlots comes from pad emissions. Holding ponds and sediment basins collect and contain the contaminated runoff from the pads and can be a source of emissions. Other sources such as manure storage and compost areas, feed storage areas, drains and collection channels, feed processing areas, and mortality storage areas are assumed to be less significant, or minor, because of their relatively small footprint and odor characteristics.

Additionally, land application activities and sites can be a significant source of odors during manure application events. However, management of these activities are solely at the discretion of the operator, and can be managed to minimize or maximize odor impact to neighboring residents. Because of the large influence that management plays in the impact of odors from these activities, and the very short time horizons these event could impact receptors, it is not considered a reasonable source to include in this process.

Method

Currently feedlot odor emissions used for modeling of odors and setback estimation tools are assumed to be constant (either an annual average or constant) in contrast to previous work and use of models by the industry. Previous work has ignored emission contributions from other production area sources such as holding ponds, sediment basins, and manure storage areas. Recent work by Nicholas et al. (2004a) has shown that feedlot emissions are a function of temperature, moisture (rainfall and runoff), surface area, and time since last event. An odor emissions model has been developed by Feedlot Services Australia Pty. Ltd. (FSA) for open feedlots that predicts the hourly emissions from feedlot pads, holding ponds, sediment basins, and manure storage areas (Atzeni et al. 2004, Nicholas et. al. 2004ab, Hudson et al., 2005). The model is comprised of two parts, the first part estimates pad moisture content, pad thickness, and pond volume using MEDLI, a feedlot hydrology model (Gardner and Davis, 1998), and a nutrient excretion model, BEEFBAL (McGahan et al., 2002). The second component uses the output from MEDLI and a meteorological file for the site to estimate the hourly emissions from production area sources. The model generates an hourly emissions file that can be used in AUSPLUME (Lorimer, 1986) or another suitable odor dispersion model to predict the hourly transport of the plume of odors from the feedlot. An outline of the process presented is shown in Figure 1 below. The results of the emissions model, along with on-site meteorological data, are input to an atmospheric dispersion model to develop odor contours (and eventually odor impact at receptor locations) near a feedlot (Nicholas et al., 2005c, D'Abreton, 2005ab). An example of the results from this process is shown in Figure 2.

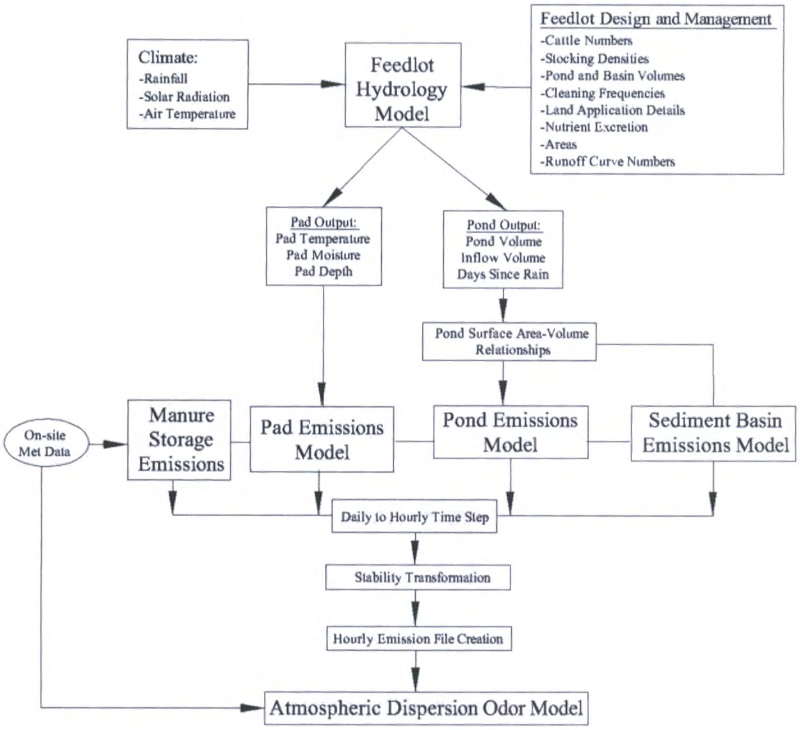

Figure 1. Process of using hydrology model to develop inputs for emissions model and then using an atmospheric dispersion model to predict odor impact

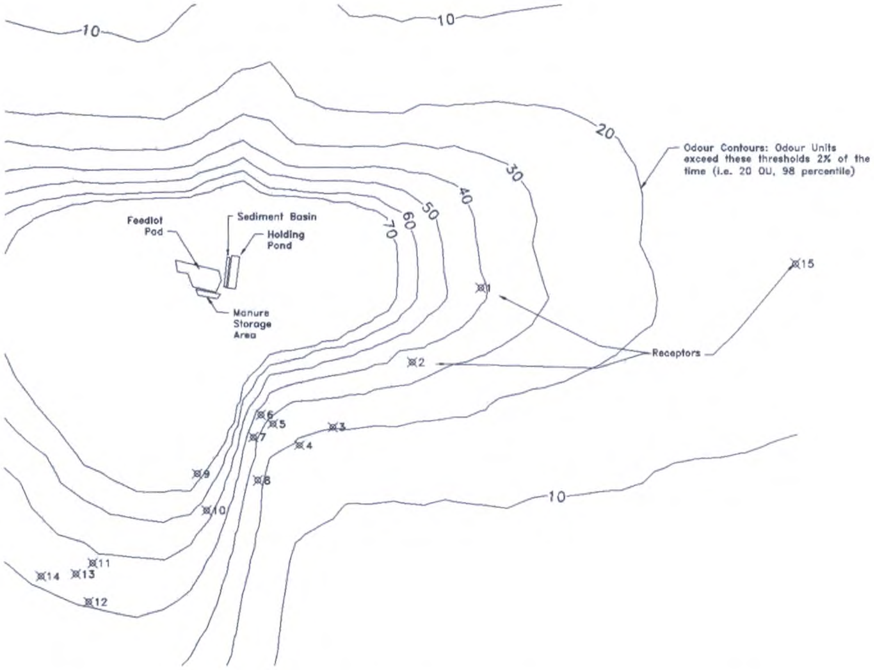

Figure 2. Example of output from AUSPLUME, showing source, receptors, and odor contours for a feedlot.

Conclusion

A process has been developed using a feedlot hydrology model to generate the needed input variables for a feedlot emissions model. A feedlot emissions model was developed from wind tunnel data that provides varied emissions based on environmental conditions for feedlot pads, holding ponds, sediment basins, and manure storage areas. The feedlot emissions model is capable of providing hourly variable emissions for feedlot pads, holding ponds, sediment basins, and manure and compost storage areas. The emissions data can then be converted to a file that can be used in an atmospheric dispersion model for evaluating odor risk for a specific site.

Using a feedlot hydrology model to derive the parameters needed to predict the variable emissions from feedlot production facilities could be used to predict the odor impact from new facilities and expansions. Additional data is needed to confirm that the feedlot pad emissions model reasonably predicts the pad emission rate for a more varied set of environmental conditions. Further work is needed to verify or ground-truth the use of the odor assessment process described above, possibly by using trained assessors, neighborhood surveys, or odor diaries. Such studies would further validate the robustness of this approach.

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Monitoring of Air Quality and Atmospheric Depositions in Background Areas in Denmark

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Abstract

Since 1989 concentrations and depositions of eutrophying air pollutants have been monitored in Denmark within the framework of the Danish Background Air Quality Monitoring Program. The program is based on a combination of measurements and model calculations with regional and local scale models. The results have shown that the average depositions of nitrogen to Danish marine waters are 10 kg N ha^{-1} and hence the atmospheric depositions contribute significantly to the large anthropogenic supply of nitrogen to the Danish marine waters. This excess supply of nitrogen leads to regular episodes with oxygen deficiencies followed by death of fish and benthic fauna. Moreover, the average annual depositions to Danish natural ecosystems are about 16 kg N ha^{-1} thereby exceeding the critical loads of many of the sensitive ecosystems. Since 1989 the total deposition of nitrogen has decreased by about 23%. This decrease is due to reductions in emissions of ammonia and nitrogen oxides in Denmark and throughout the rest of the European countries.

Introduction

During the last decades the air quality and the deposition of various air pollutants have been monitored in the Danish Background Air Quality Monitoring Program. The overall goal with the program is to determine the present state of the air quality in background areas in Denmark and to quantify the deposition of air pollutants to Danish marine waters and natural ecosystems. Moreover, it is the aim to measure long-term trends in concentrations and depositions in order to evaluate effects of national and international efforts to reduce air pollution. Finally, it is the aim to fulfil the national and international requirements for background monitoring in Denmark. The program is based on a combination of measurements at a network of stations and model calculations with both regional scale Eulerian models and local scale Gaussian plume models. The measurements are used for determination of the actual state of the air quality and deposition and the long-term trends. The model calculations are mainly used to estimate the depositions to larger geographical areas and the influence of the various sources of air pollutants and their origin. Moreover, local scale model calculations are also used for determination of nitrogen deposition to selected natural ecosystems.

The program covers eutrophying and acidifying air pollutants, heavy metals, ozone, and selected organic compounds as pesticides, PAH and nitrophenols. However, at present the main focus is on eutrophying nitrogen compounds originating from both national and international emissions of ammonia and nitrogen oxides. The deposition of these compounds has large impact. The air pollution originating from agricultural activities related to the large production of livestock in Denmark is of special interest. The annual Danish emission of ammonia was 80,000 tons nitrogen in 2003 (Illerup et al., 2005) corresponding to roughly 15 kgN per capita. Denmark is therefore one of the European countries with the largest emission of ammonia per capita. This paper presents some of the main results from monitoring of air pollution with nitrogen compounds during the last 17 years.

Methods

The network of measurement stations consist of 6 stations for measurements of the concentration of nitrogen gases and particles and 8 stations for measurements of the wet deposition of ammonium and nitrate (Figure 1). All the stations are situated in Danish background areas in order to obtain measurements representing the background levels for that area rather than the impact of a local strong source.

The diurnal sampling of nitrogen gasses and particles is carried out with the Danish filter pack sampler which is a slight modification of the filter pack sampler used in EMEP (EMEP, 2004). The filter pack sampler is normally used for sampling of the sum of ammonia and particulate ammonium together with the sum of nitric acid and particulate nitrate (referred to as total nitrate). However, parallel measurements using denuders and filter packs have shown that the filter pack can give a reasonable separation between ammonia and particulate ammonium under Danish conditions. Hence the results are given separately for ammonia and particulate ammonium. The diurnal concentrations of nitrogen dioxide are measured using NO_x-monitors at two stations and a NO_2-sampler based on sampling on potassium iodide coated glass filters on one station (EMEP, 2004).

The wet deposition of ammonium and nitrate is sampled on half-monthly basis using standard bulk samplers comparable to the samplers used within EMEP (EMEP, 2004). Double or triple sampling is used at all the stations in order to reduce uncertainties especially from contamination of the samples.

Aqueous extracts of the filters and the precipitation samples are analyzed for the nitrogen compounds using ion chromatography and automatic spectrophotometric techniques.

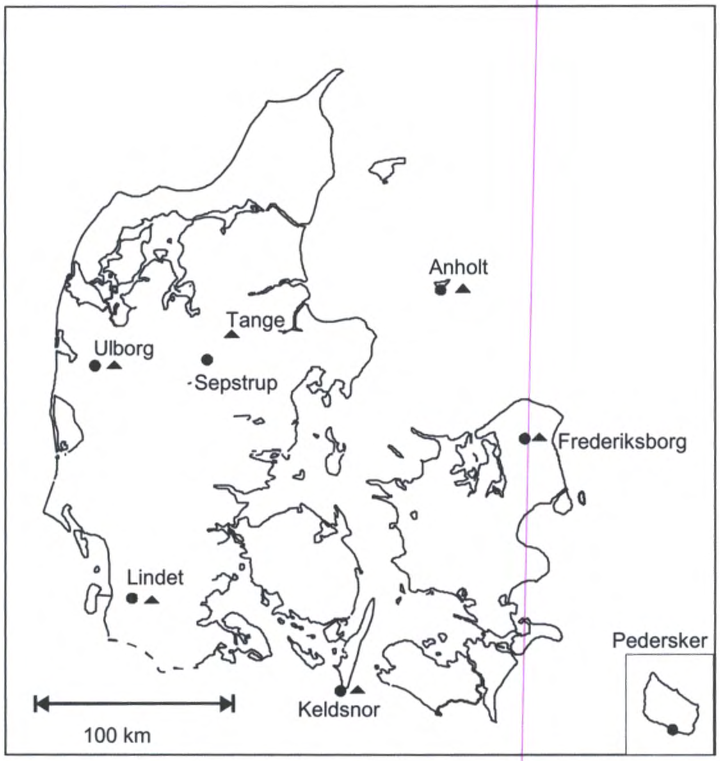

Figure 1. Measurement stations in the Danish Background Air Quality Monitoring Program used for measurements of nitrogen containing gasses and particles ( ) and wet deposition of ammonium and nitrate ( ).

The regional scale model calculations of the nitrogen depositions are carried out with the Danish Eulerian Hemispheric Model (DEHM) which is a three dimensional Eulerian model covering the Northern Hemisphere (Christensen, 1977; Frohn, 2004). DEHM contains three nests with increasing resolution in order to make calculations for the Danish marine waters and land surfaces with a resolution of 16.67 km x 16.67 km. The meteorological input data are calculated using NERIs version of the meteorological mesoscale model MM5v2 (Grell et al., 1995). Emissions are a combination of several sources, where source and distribution in time and space is described by Hertel et al., (2002). The emission inventories for Europe are based on data from EMEP with a geographical resolution of 50 km x 50 km (EMEP, 2005). The annual total emissions for Danish sources are produced at NERI and the geographical distribution of the emissions of NH3 is based on an emission inventory with a geographical resolution of 1 km x 1 km (Illerup et al., 2005; Ambelas Skjøth et al., 2006).

NERI has also developed a local scale model OML-DEP for detailed calculations of the nitrogen deposition to selected natural ecosystems. The model is based on the Danish OML model, which is a Gaussian dispersion model (Olesen et al., 1992). This OML-DEP model can handle point and area sources and has been formulated for calculation of the dry deposition of ammonia using the Surface depletion principle (Horst, 1977). The model domain used in connection with the monitoring program is 16 km x 16 km with a geographical resolution of 400 m x 400 m. The model takes into account the medium to long-range transport of ammonia from the regional scale model DEHM. The local scale model uses a subset of meteorological input data generated by MM5v2 for use in the regional scale model. The local land use affects the deposition via associated turbulence and deposition velocity. The calculation on local scale is based on a special emission inventory for the Danish emissions of ammonia with a geographical resolution of 100 m x 100 m and division into area and point sources (Gyldenkærne, 2005).

Results and Discussion

The model calculations have shown that the nitrogen deposition to the Danish marine waters on average was about 10 kg N ha^{-1} in 2004 (Figure 2). The deposition is highest in the southern part of the Danish marine waters due to areas with high emissions of nitrogen oxides and ammonia in the countries south of Denmark. The total input of nitrogen to the Danish marine waters is about 100,000 tons nitrogen per year. It has been calculated that the atmospheric depositions to the inner Danish waters (Kattegat and Belt Sea) contribute with up to one third of the total nitrogen load from surrounding land and atmosphere (Ærtebjerg et al., 2003). Hence the atmospheric deposition contributes significantly to the general supply of nitrogen to the inner Danish waters. The large supply of nitrogen has been one of the main reasons for the regular episodes with oxygen deficiencies and subsequent death of fish and benthic fauna, which have been observed in these waters during the last decades (Ærtebjerg et al., 2003).

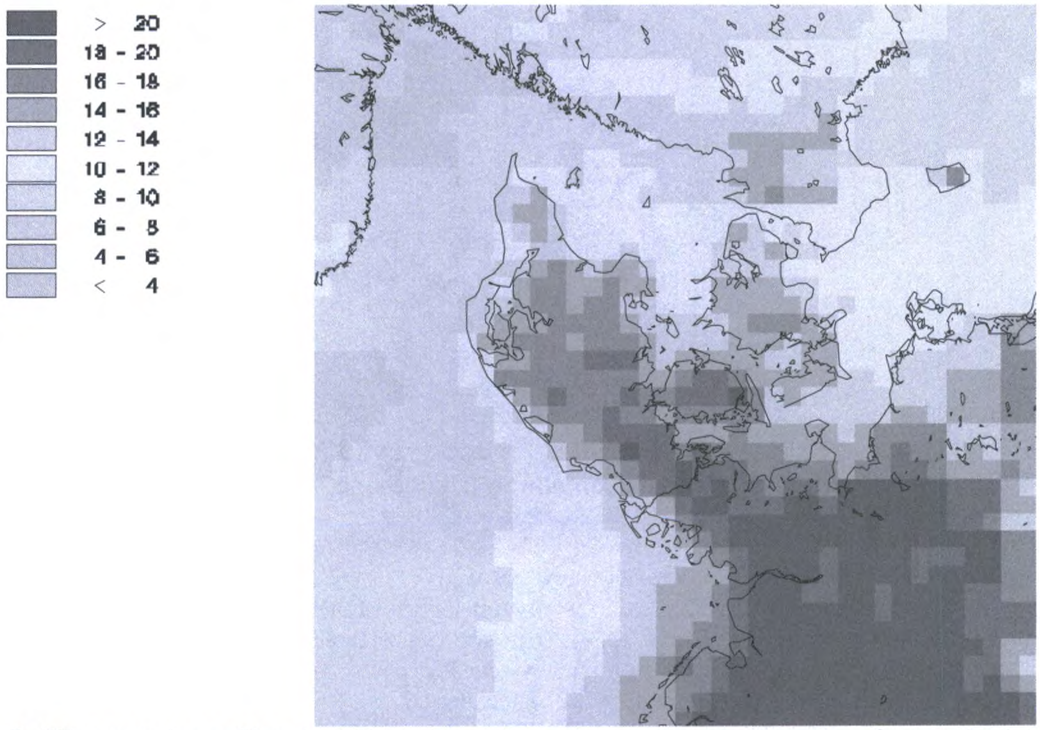

Figure 2. Nitrogen deposition in 2004 to Danish marine waters and land surface calculated using DEHM. The units are kg N ha^{-1}.

The model calculations have shown that the nitrogen deposition to the Danish land surfaces on average was about 16 kg N ha^{-1} in 2004 (Figure 2). The highest depositions are seen in the south western part of

Denmark due to high density of animal husbandry, high precipitation and short distance to major emission areas in the countries south of Denmark. Hence the deposition is above the critical loads for many of the sensitive Danish ecosystems e.g. heath and bogs (Bak, 2001). This finding is in agreement with the observation of a decline of the coverage and quality of these ecosystems in Denmark (Bach et al., 2005).

As an example, Figure 3 shows the results from local scale model calculations of the deposition of ammonia to Randbøl Heath which is situated in the central part of Jutland (the peninsula in the western part of Denmark). The total deposition of nitrogen to the heath is 14-15 kg N ha^{-1} of which 2-3 kg N ha^{-1} is due to ammonia and 12 kg N ha^{-1} is due to medium to long range transport of nitrogen containing compounds. The critical load for nitrogen deposition to heath in Denmark is 10-15 kg N ha^{-1} (Bak, 2003). During the last 17 years there has been a significant decrease in the nitrogen deposition (Figure 7) and it is therefore most likely that the critical load has been exceeded for decades at Randbøl Heath.

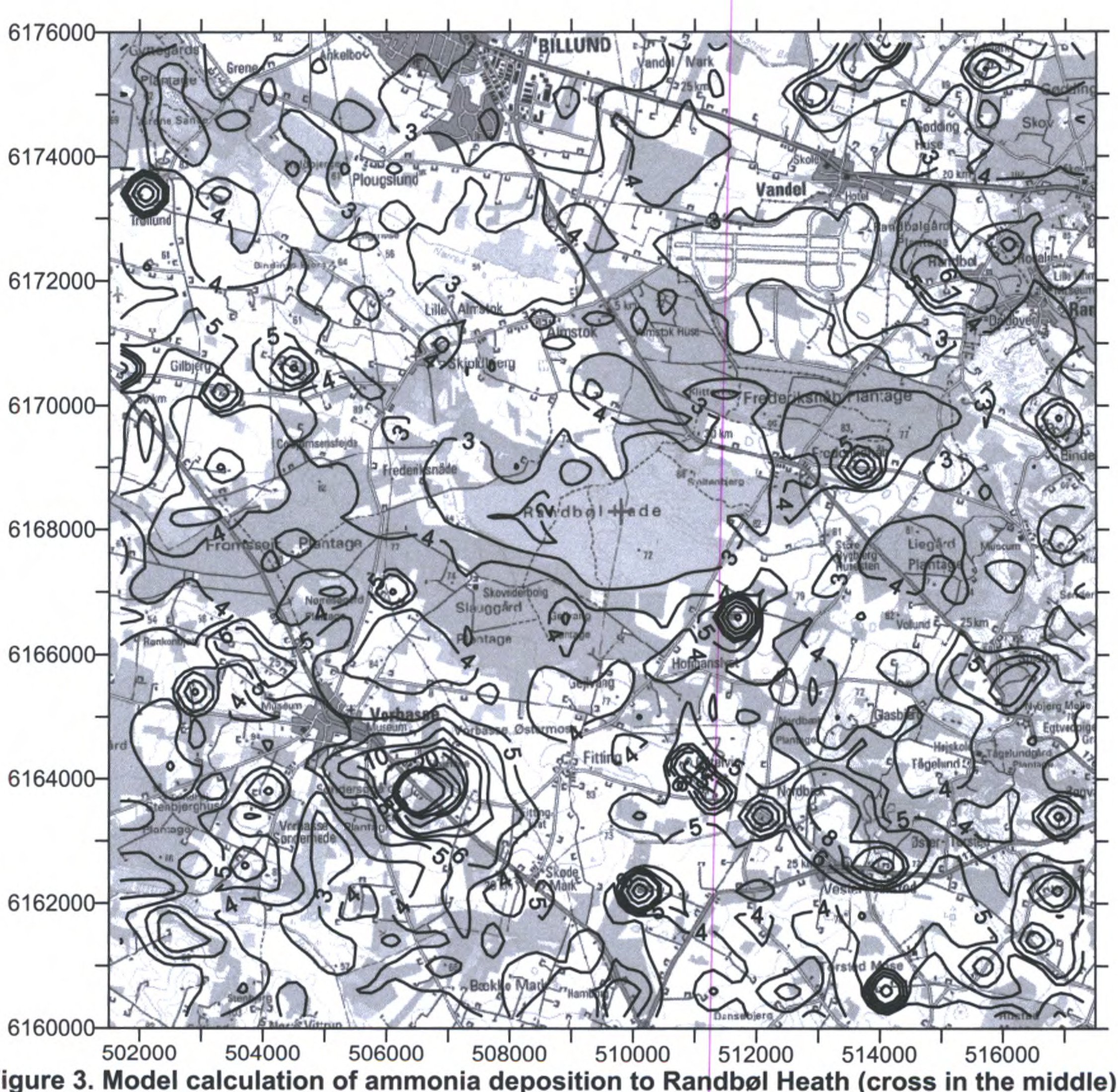

Figure 3. Model calculation of ammonia deposition to Randbøl Heath (cross in the middle). The calculations are carried out with the local scale model with a geographical resolution of 400 m x 400 m. The numbers on the axis corresponds to the UTM 32 coordinates in meters. The numbers on the contour lines corresponds to the ammonia deposition and is given in kg N ha^{-1}.

Recently the last fifty year's change in the vegetation at Randbøl Heath has been characterized on the basis of air photographs (Degn, 2006). This work has shown that the coverage with heath plants and other dwarf bushes has decreased from 90% in 1954 to less than 15% in 2005. Simultaneously the coverage with nitrophilous grasses (*Molinia coerúlea* and *Deschámpsia flexuósa*) has increased and taken over the heath. The high atmospheric deposition of nitrogen at Randbøl Heath is believed to be one of the major reasons for this change (Degn, 2006).

Model calculations have shown that air pollution from Danish sources is responsible for about 45 % of the total nitrogen deposition in Denmark. Of this 40% comes from agriculture and only 5% from various combustion processes (Figure 4). The remaining parts (55%) comes from long range transport of reduced and oxidized nitrogen from agriculture and combustion sources in other countries; mainly from countries south and west of Denmark. It is therefore evident, that the problem with high nitrogen supply to Danish marine waters and natural ecosystems has to be solved on an international level and that agriculture in Denmark as well as the other European countries is the main source of atmospheric nitrogen deposition in Denmark.

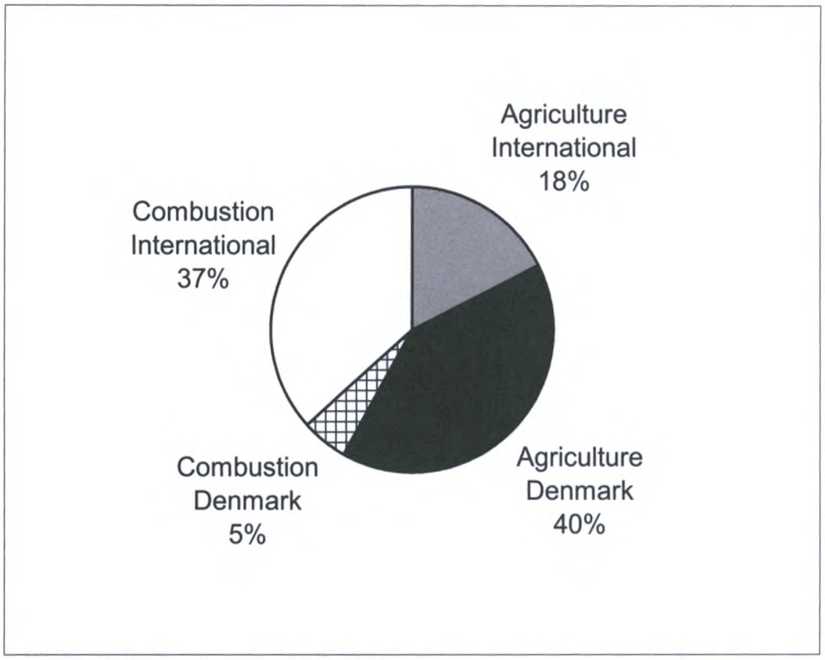

Figure 4. The contribution of Danish and international sources to the deposition of nitrogen in Denmark in 2004. The deposition is also divided in nitrogen due to agriculture and combustion processes.

The measurements have shown that the concentrations of particulate ammonium and total nitrate have decreased significantly at all the stations (Figure 5). The average decrease since 1989 is 42 and 29 % for particulate ammonium and total nitrate, respectively. The long-term trend for ammonia varies considerably from station to station due to varying influence from local sources. There is a tendency for a decrease in the long-term trend of the ammonia concentration at all six stations. However, the decrease is only significant at one of the stations. On average the decrease is about 20 % since 1989.

The observed pattern with a small decrease in primary ammonia and a large decrease in secondary particulate ammonium may be explained by the interaction with the atmospheric sulfur compounds. Since 1989 there has been a statistical significant decrease in sulfur dioxide (90 %) and particulate sulfate (60 %) in Denmark (Ellermann et al., 2005). As a consequence the atmospheric lifetime of ammonia may have increased since the chemical conversion from ammonia to particulate ammonium has been slowed down due to the decrease in the reaction with particulate sulfate. This can explain the observations of a small decrease in ammonia and a large decrease in particulate ammonium.

The wet deposition of both nitrate and ammonium has decreased since 1989 with 12 and 29 %, respectively (Figure 6). Averaged over all the stations the change is statistically significant for ammonium but not for nitrate. However, there is a tendency for a decrease in wet deposition of nitrate at all stations. This decrease in wet deposition has been measured despite, that there has been an increase in the precipitation at five out of six stations.

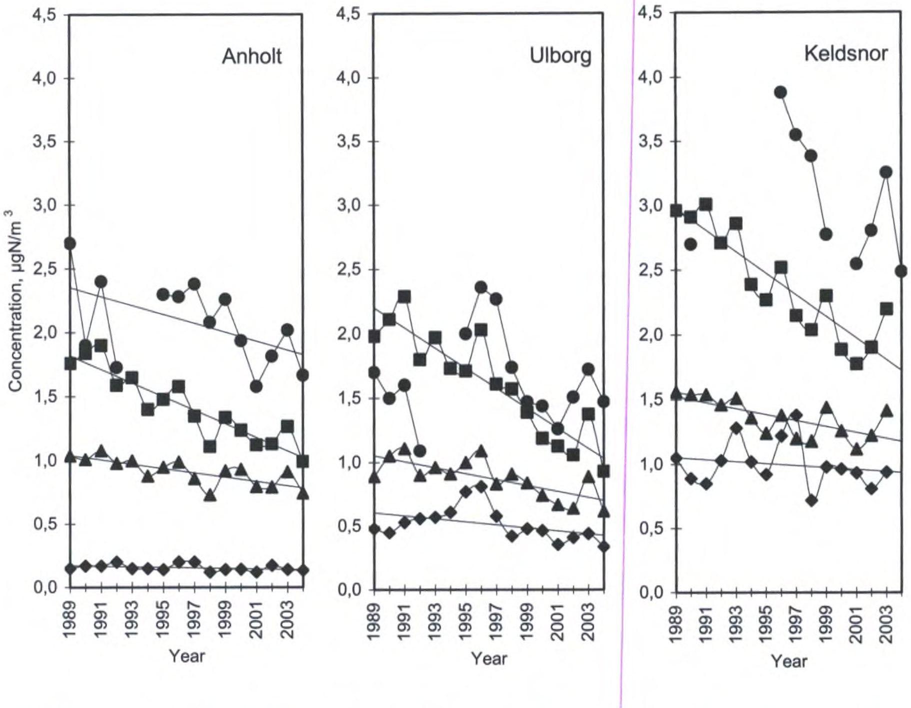

Figure 5. Long-term development in nitrogen concentrations at three of the Danish main stations: Anholt, Ulborg, and Keldsnor. ( ) Nitrogen dioxide, ( ) particulate ammonium, ( ) sum of nitric acid + particulate nitrate, ( ) ammonia.

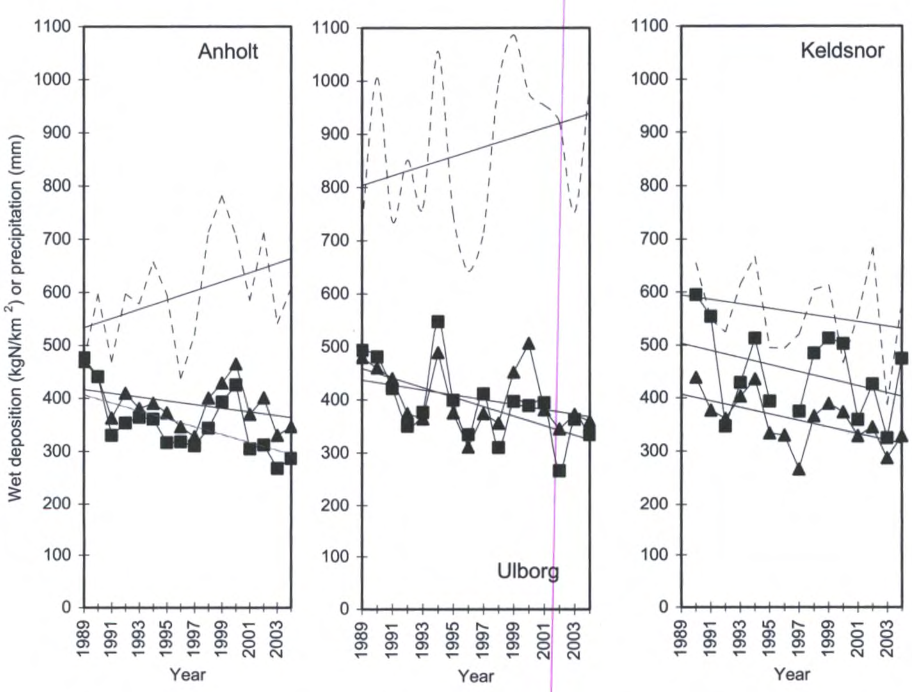

Figure 6. Long-term development in wet depositions of nitrogen at three of the Danish main stations: Anholt, Ulborg, and Keldsnor. Precipitation (dashed line), ( ) ammonium, ( )

nitrate.

The long-term trends in both concentrations and wet depositions of nitrogen can readily be explained by the reductions in the emissions due to international and national action plans (EU directive for National Emission Ceilings, Gothenburg Protocol, Danish Action Plans for the Aquatic environment etc.). In Figure 7 it is shown that the relative decrease in the nitrogen deposition in Denmark follows the relative decrease in the emission of nitrogen in the European Union and Denmark. Approximately half of the nitrogen depositions can be attributed to Danish sources and half to long range transport. It is therefore evident that the efforts in order to reduce emissions in Denmark as well as in the rest of the European countries have lead to significant changes in the nitrogen deposition.

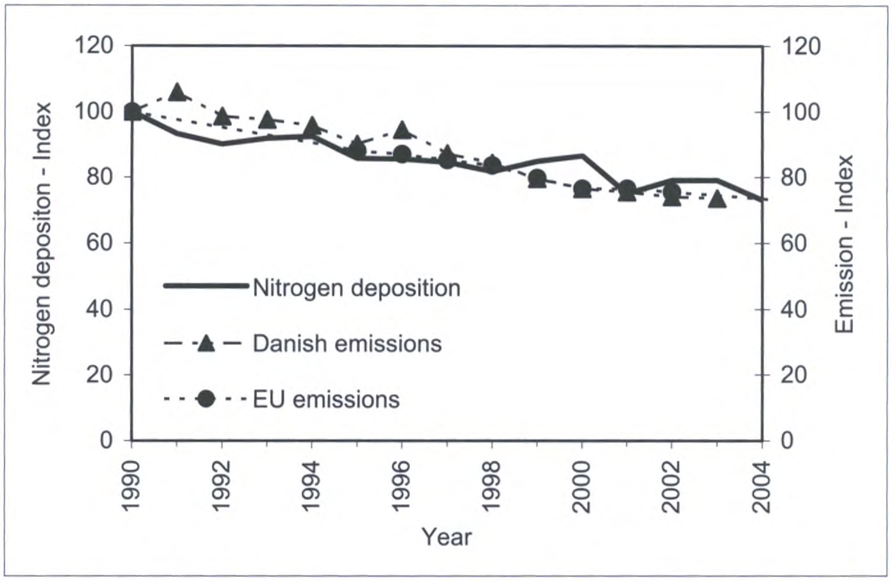

Figure 7. Comparison between the long-term trends in nitrogen deposition and emissions from Danish and European sources (EU). The trend in nitrogen deposition is calculated as the average for the six main monitoring stations. Deposition and emissions are given relative to 1990. (Illerup et al., 2005; EMEP, 2005)

Conclusions

Long-term monitoring of the air quality and depositions to Danish marine waters and natural ecosystems has documented that the nitrogen deposition in Denmark is high compared to critical loads for many of the sensitive Danish ecosystems, and the deposition contributes to the eutrophication of the Danish marine waters. Moreover, the monitoring program has shown that it is beneficial to use a combination of measurements at fixed stations and model calculations in order to get a better understanding of the observations and the processes determining the size of the nitrogen deposition in Denmark. Finally, the measured decrease in the long-term trend for the nitrogen deposition has shown that the work with reduction of emissions has lead to significant results. However, further reductions in the emissions may still be needed in order to protect the Danish nature and ensure high bio diversity in the country.

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Effects of Technologies for Reducing Ammonia Pollution from Agriculture: Outline of an Environmental-Economic Framework

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Abstract

The aim of the poster is to present a joint methodology for applying models and data for supporting policy decisions and advisory services with respect to handling ammonia emissions from livestock production and the depositions resulting from these emissions. The full chain of pressures and effects encompassing the link between production activities and welfare effects is subject to analysis enabling quantitative cost-benefit analysis. The possibilities for integrating spatial agricultural data with geographically targeted models of costs and benefits are discussed including links to models of emissions, transport, and localized loads and exposure. The components of the socio-economic analysis are discussed in terms of cost analysis and benefit transfer enabling CBA of site specific changes in air emissions and the resulting welfare effects. By developing and analyzing scenarios both reflecting differences in abatement technologies and localization of the livestock production, a range of costs and benefits can be explored for different abatement technologies that will assist policy makers in targeting policies. The poster describes the methodological framework and the current status of knowledge and identifies issues for further research.

Introduction

Agricultural livestock production and the resulting air emissions may cause welfare losses because of odour problems to neighbors and ammonia depositions to protected nature areas (EEA, 1995). Therefore, odour problems are addressed in the Third Aquatic Action Plan and ammonia emissions are subject to regulation internationally in the EU National Emission Ceilings Directive and Gothenburg protocol and in the National Ammonia Action Plan.

However, the scale of the problems is a result of a complex interaction between the size, location and production technology of livestock farms, emissions and transport, and the exposure of the recipients (urban settlement and protected nature areas). In Denmark agricultural husbandry production is intense in some regions, and local ammonia emissions add significantly to the deposition of transboundary nitrogen. Total nitrogen deposition varies between county averages of 17-24 kg N ha^{-1} y^{-1} but may be as high as 100-200 kg N ha^{-1} y^{-1} near large husbandry farms. The effects on odour problems are realized but the techniques for quantifying these are yet to be applied and validated in practical use. With respect to the effects on nutrient poor nature sites the deposition of nitrogen exceeds the critical loads of many nitrogen poor ecosystems. In 1999 the critical loads were projected to be exceeded for all Danish bogs and oligotrophic lakes (*Littorelletalia uniflorae*), 94% of coniferous forests, 63% of deciduous forests, 57% of dry grasslands, 42% of inland heath lands and 7% of coastal dune heaths (Bak et al., 1999).

One of the major policy questions with respect to nature protection in Denmark and northern Europe is the possibility for reducing ammonia loads. The complexity of the emission and deposition patterns and the dispersed location of nitrogen sensitive nature areas pose a demanding task for policy analysis. This is because significant contributions to loads derive both from local, national and international sources as well as the varying critical loads between different locations.

The reduction of eutrophication and acidification effects from air pollutants was included in the form of explicit targets in the recent impact assessment of the Thematic Strategy for Air Pollution by the EU Commission (EU Commission 2005). Given the course resolution of the RAINS model's grid cells (50*50 km) and the site-specific character of potential benefits from emission reductions, no attempt was made to quantify the benefits in monetary terms.

In order to support policy decisions and give recommendations to cost-efficient abatement strategies, this chain needs to be quantitatively modeled, encompassing the site-specific aspects of the problem. Therefore, development of analytical tools linking economic models, emission models, and models of deposition and critical loads is needed to identify cost-efficient strategies for complying with the international agendas for protecting nature and biodiversity.

Methods

Agricultural Data

The site specific nature of both the emission sources and the recipients, *in casu* the nutrient poor ecosystems, implies that policy analysis needs to be site specific in order to identify cost-efficient strategies for reducing ammonia loads from agriculture. Therefore, the starting point of the analytical framework is a site-specific description of the agricultural production with emphasis on livestock production in terms of the location of stables, storage facilities for manure and the crop areas where manure is applied. This is done based on the in a GIS by using digitized maps of the location of agricultural field blocks based on the General Agricultural Register (GAR); and location of farm buildings and husbandry based on the General Husbandry Register (GHR). Both agricultural registers are geo-referenced and developed in order to control farmers eligibility to receive EU hectare and husbandry premiums. For each farm unit data on land use and livestock hold are recorded in the register, and the initial ammonia emission from each farm is estimated as part of the Danish emission inventories (Mikkelsen et al., 2005).

Cost Estimates and Emissions Reductions

Based on the geographically distributed agricultural data it is possible to identify technologies relevant for reducing ammonia emissions. The technologies are analyzed with respect to their financial economic costs and effects on ammonia emissions (NH_3-N). Effects on ammonia emissions are estimated based on practical tests, typically performed by the Danish extension center as part of the identification of Best Available Techniques (EU Commission, 2003; for a Danish reference see www.lr.dk). The costs are estimated in annualized values comprising both investments, maintenance and running costs and benefits in terms of increased nitrogen content in the manure and, subsequently reduced need for fertilizer input (formula 1).

$$AC_i = IC_i + MC_i + RC_i - NV_i$$

where

AC_i is the annual abatement costs of technology *i*,

IC_i is the annualized investment costs (interest and deprecations) of technology *i*, ,

MC_i is the maintenance cost of technology *i*,

RC_i in the annual running costs (input and labor) of technology *i*,

NV_i in the benefits in terms of increased nitrogen content in the manure of technology *i*.

In table 1 examples of abatement technologies derived from an ongoing analysis are given.

By relating the abatement technologies to the different types of livestock production it is possible to evaluate the consequences of different scenarios in terms of costs and reduces ammonia emissions. As the farm data are geo-referenced the scenarios can be developed to reflect both the type of livestock production, the location of the production ant the various abatement technologies, thus, addressing a wide number of policy-relevant dimensions. One example of using the framework in policy analysis are reported on Schou et al. (2006) demonstrating the effect of establishing buffer zones to reduce ammonia loads to nature areas.

Table 1. Financial economic costs and emissions reductions resulting from abatement technologies in stables.

	DKK/kg N	DKK/AU[1]	NH_3-N red.
Acidification of manure from slaughter pigs	55	615	70%
Cooling of manure from slaughter pigs	69	688	40%
Chemical air cleaning in pig stables.	42	367	64%
Acidification of manure from dairy cows	119	433	50%
Drying of manure from hens	37	247	60%

1. AU: Animal Unit; One AU correspond to a yearly production of 100 kg N in manure.

Modeling of Deposition Patterns

However, in order to quantify the full chain of driving forces and effects related to agricultural ammonia emissions modelling of transport and deposition of ammonia needs to be included. At NERI a regional scale Eulerian model DEHM-REGINA is applied for calculating atmospheric background depositions of nitrogen to Danish nature. The local scale plume model OML-DEP is applied for computing nitrogen depositions from single farms (barns, storage tanks and evaporation from fields in connection with manure application) to the nearby area within a few km from the farm. These two models are operated as routine tools within the Danish background monitoring programme, and furthermore they are combined within the DAMOS (Danish Ammonia Modelling System) model system for assessment of total nitrogen loads in the vicinity of livestock farms (Hertel et al. 2006). The national Guideline for regulating ammonia from livestock farms in Denmark is currently under revision, and the future Guideline will be based on OML-DEP and DEHM-REGINA and the DAMOS system. Local ammonia emissions are calculated from Agricultural field blocks based on GAR; and location of farm buildings and livestock is based on GHR. Standard emission factors are obtained from a Danish norm system. A methodology for deriving a detailed seasonal variation in emissions has been developed and applied in the models (Ambelas Skjøth et al., 2004; Gyldenkærne et al., 2005). Application of the detailed seasonal variation has improved the model performance considerably. Model calculations have shown than typically a little more than 20% of the ammonia emission from local livestock farms is deposited within a radius of 2km from the farm.

Benefits of Reduced Deposition and Odour Problems

Knowing the changes in depositions and the exceedense in the critical loads for various nature types and the exposure of odour to individual households, the last step in a CBA is to estimate the monetary benefits from the changed effects. The empirical work on valuation of non-marketed goods does not enable valuation of such site-specific effects. Therefore research is needed both in terms of sampling of primary data to be used for estimating preferences for changes in biodiversity protection and changes in exposure to odour from livestock production, and in terms of developing benefit methods for generalized used of the results. One example related to odour problems could be undertaking a case study using stated preference and hedonic pricing methods for estimating neighbors' perceptions and valuation of odour problems from pig production. Results from the stated preference method in terms of willingness to pay for avoiding odour problems can be transferred to the case study. This is done by adjusting the primary results to the study area based on information about the socio-economic background of the population such as average income, percent of newcomers from urban areas, percent of residents with personal relations to animal farms, etc. The hedonic pricing results can be implemented in a regionally differentiated hedonic price model, which describe odour impact on house prices corrected for other housing and local characteristics. Together with information on house prices and house locations the hedonic price model allows the estimation of welfare losses from odour impacts for individual households in the different scenario settings.

Conclusions

The overall aim of this poster is to establish a joint framework for applying models and data for supporting policy decisions and advisory services with respect to reduce eutrophication of nitrogen poor nature types and handling odour problems from livestock production. The framework is designed to facilitate the use in practical policy analysis and will be demonstrated by analysis of costs and benefits of technology scenarios for abating odour problems from livestock production in a case study area. The system should be based on a GIS and couple spatial agricultural data with models of emissions, transport, and localized loads, and further, include socio-economic components enabling CBA of site specific changes in air emissions and the resulting effects. Analysis should focus on developing and analyzing a range of scenarios both reflecting differences in abatement technologies and localization of the livestock production, a range of costs and benefits are explored which will assist policy makers in targeting policies to yield the most welfare improvements.

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Footprints on Ammonia Concentrations from Emission Regulations

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Abstract

Ambient ammonia concentrations are priamrily related to agricultural activities. In this paper a simple ammonia emission model is presented and used for analyzing 15 years of ambient ammonia concentrations from Denmark. The emission model is used for explaining changes in observed concentrations as a result of changed agricultural practice enforced by national regulations.

Introduction

Ammonia is a waste problem in areas with large agricultural activity. The surplus of fertilizer associated with agricultural activities affects rivers, coastal waters, terristial ecosystems, and may e.g. cause an irreversible death of our forests (Nosenga, 2003). Effects of high nutrient loads are already seen in USA and Europe (Nosenga, 2003) and recently it has been estimated that 60% of the European ecosystems have exceedances of their critical level of nutrient load (Bak, 2001).

Reduction initiatives such as the Goethenburg protocol aims at reducing emission of air pollutants into the atmosphere. Depending on reduction methods and constraints laid on farming practice, changes may be observed in ambient concentrations as a result of the applied reduction strategies. Here we present and explain the air quality changes in Denmark related to Danish agriculture during a 15 year transition period from a period with almost no regulations to a period with a vast amount of regulations.

Two thirds of the Danish land areas are applied for agriculture, and the environmental problems associated with the surplus of fertilizer have been observed for decades. The surrounding coastal waters had already in the 1980s frequent algae blooms, followed by low oxygen levels at the bottom waters: In extreme cases causing a subsequent death of fish and benthic fauna (Conley et al., 2002, Ærtebjerg et al., 2003). As a consequence, three national aquatic action plans have been implemented in Denmark. The main purpose of these action plans is to reduce the load of (eller input of ?) nitrogen to the marine waters, ground water, lakes and streams through the implementation of a large number of ammonia reduction methods (Grant et al. 2004). Regulations have gradually been introduced during the 1990s and have forced the Danish farmers to change their practice especially with regard to the handling of manure. This paper presents an ammonia emission parameterization for the different agricultural sources. The model will be used for explaining variations and trends in ambient ammonia concentrations in Denmark during 15 years. Finally the results are discussed and conclusions will be drawn.

Measurements

Diurnal concentrations of several atmospheric components including NH_3 have been measured during the period 1989-2003 and reported annually as part of the Danish national air quality monitoring program (e.g. Ellerman et al., 2003, 2004, 2005) initiated to follow the impact of the national action plans. Measurements of the ammonia concentration are carried out using the filter pack method as described by Ambelas Skjøth et al. (2004). Five monitoring stations are land-based and one is located in the middle of the Kattegat Sea (Ellermann et al., 2006).

The measured seasonal pattern of ammonia concentrations at the land based background stations has been changing during the entire measuring period. A change, which until now, has remained unexplained. Here we present the results from the station located at Tange (56° 21' N, 9° 36' E). The time series from the other land based stations show a similar seasonal pattern, although the annual trend is not as significant as seen in Tange.

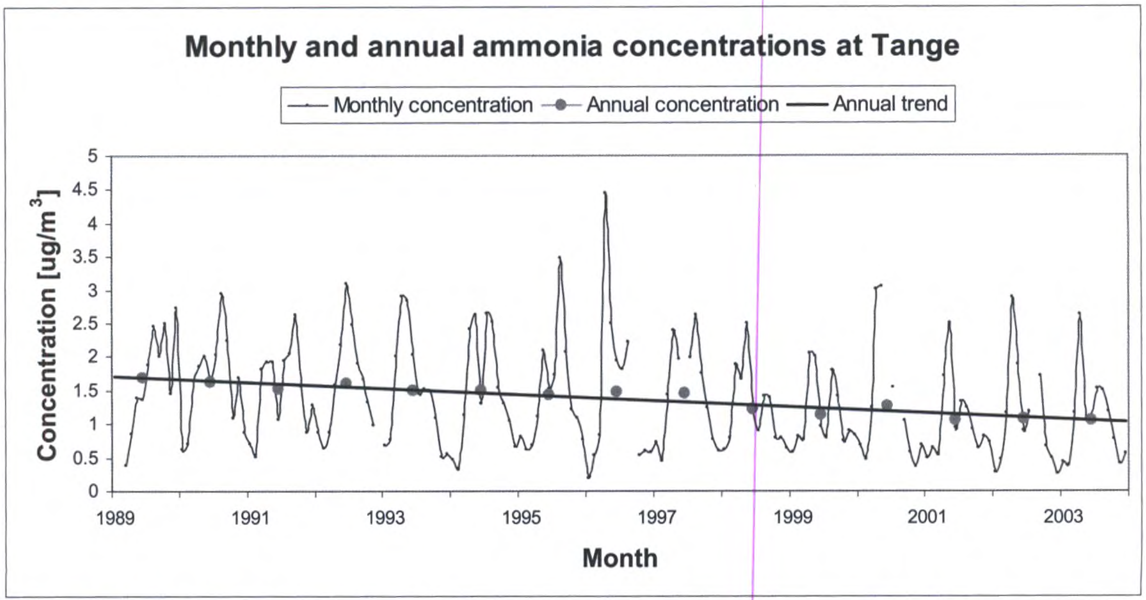

Figure 1. Monthly and annual ambient ammonia concentrations measured at Tange.

The measured seasonal pattern and the annual ambient mean concentration of ammonia has changed during the years 1989-2003. During the first years, the concentration is generally high during summer and moderate peaks are seen during spring and autumn. The last years the summer and autumn level has decreased while the spring level has increased. Furthermore, there is a decreasing trend in the annual ammonia concentrations, where the trend at the station near Tange is statistical significant on a 95 % confidence level.

Description of the Emission Model

The emission model has been developed with the requirements of on the one hand being relatively simple but on the other hand also be able to describe the main variations in ammonia emission during the year. Furthermore the parameterization should be able to handle changing agricultural production methods and finally it should be possible to implement the parameterization in local and regional scale models.

Therefore, to fulfil these demands, a parameterization based on several submodels have been developed (Gyldenkærne et al., 2005, Ambelas Skjøth et al., 2004). Each sub model handles a group of ammonia sources within the agriculture. These main groups can separated into buildings, grown crops, application of manure and mineral fertilizer, grazing animals and other sources. Figure 2 shows an example of the temporal variation of ammonia from these groups.

The model takes into account differences in volatilization of ammonia due to temperature differences. Therefore, the temporal variation of ammonia differs between different types of buildings (Figure 2 left). Furthermore, application of manure and artificial fertilizer is applied several times during the year (Figure 2 right), where application time depends on plant growth. Therefore, date of application changes between years and geographical location.

Model results

The emission model requires an overall annual emission inventory and local meteorological data. Data may be obtained from measurements or as in this case, results from the non-hydrostatic numerical weather prediction model MM5 (Dudhia, 1993), which is applied as meteorological driver for the hemispheric transport-chemistry models at NERI (Heidam et al., 2004).

In Denmark the geographical location of each agricultural building such as stables and storage and the number of animals associated to the location are stored in central databases. Furthermore, information about individual fields associated to the production facilities is also available. Each production facility has due to the legislation introduced in the early 1990s estimates of the input and output of nitrogen during each of the stages in the production line. Therefore, it is possible to produce highly detailed annual ammonia emission inventories, which may be sorted into different sectors of the agricultural production (Ambelas Skjøth et al., 2004). A graphical example of these inventories is given in Figure 3.

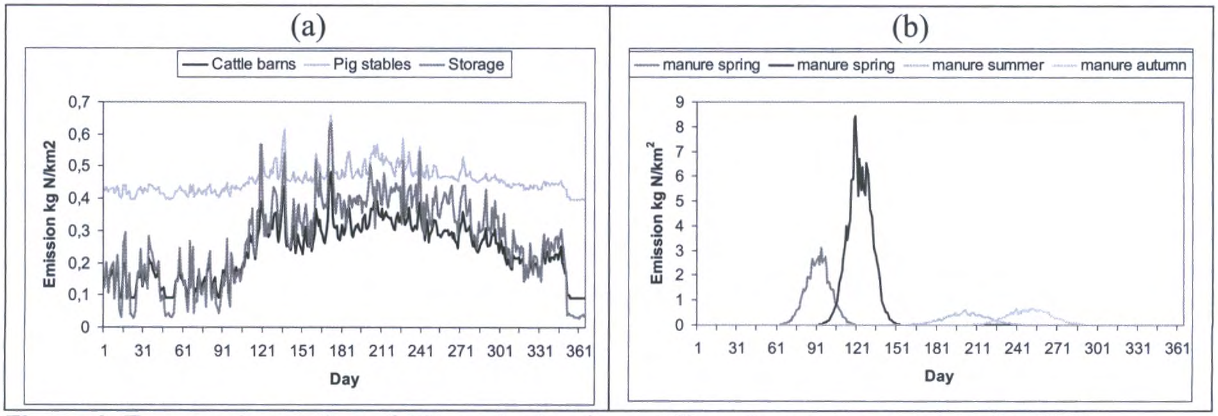

Figure 2. Temporal variation of NH_3 emission from different source groups in the NH3 parameterization. Calculations are in [kg N/km^2] for the Tange area. Emission calculations are from buildings and storage(a) and from field applications of manure(b).

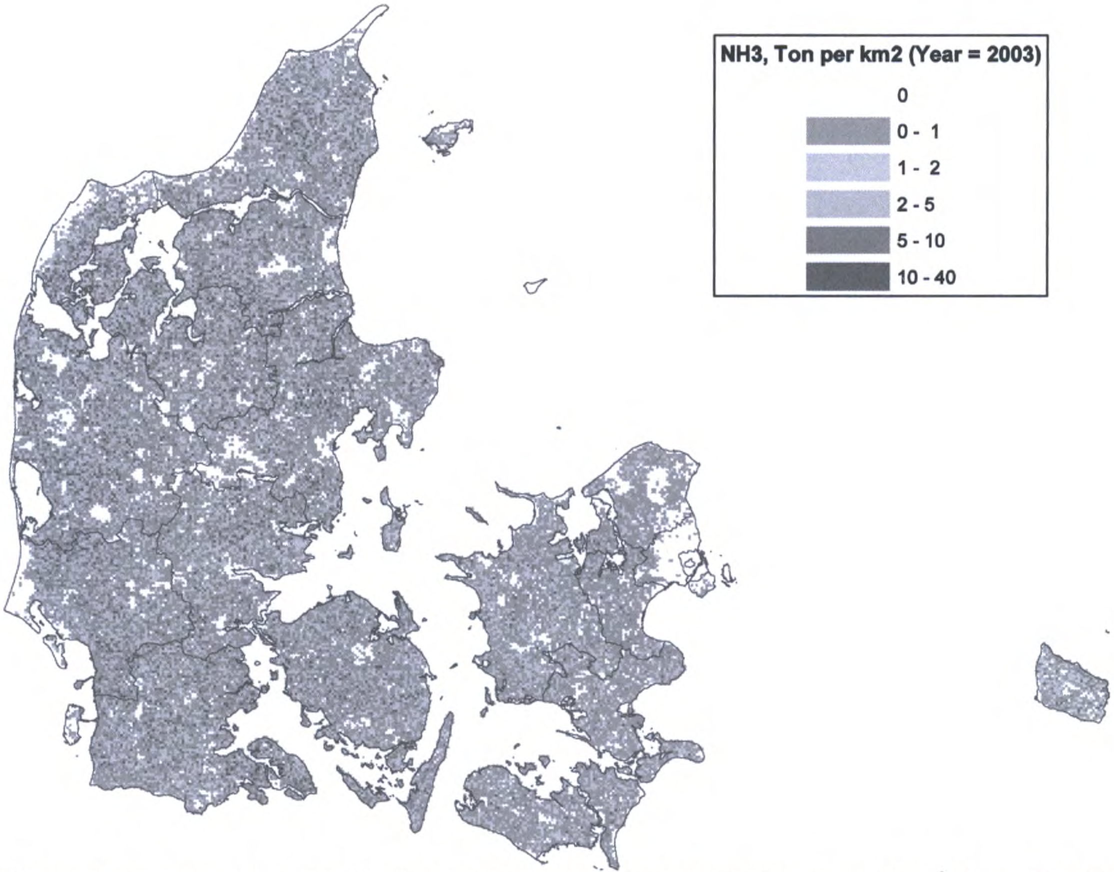

Figure 3. Geographical distribution of the annual NH_3 emission [Ton N/km^2] from Danish agriculture distributed in a 1 km x 1km grid for the year 2003.

Figure 3 shows the geographical distribution of the total annual emission for the year 2003 on a 1 km x 1 km grid. Similar inventories have been made for 12 different agricultural categories for the years 1985 - 2003. The areas with high emissions marked by red spots are scattered throughout the country and the western part of the country generally has a higher emission density than the eastern part. The annual national emission for the different agricultural categories for the years 1985, 1990, 1995, 2000 and 2003 are presented in Table 1.

There is no central statistical information concerning application methods of manure. Therefore questionnaires among 15% of all Danish farmers are used as a basis for information about application methods in Denmark during the years. Use of mineral fertilizer at field level is based on a method described in Ambelas Skjøth et al., (2004), by combining the national consumption of mineral fertilizer within the agricultural industry, the plant need of fertilizer at field level subtracted by the applied amount fertilizer from husbandry, which again depends on the available manure at farm level.

The emission is distributed in categories (Table 1): emission from buildings, storages, grown crops, emission due to application of manure and mineral fertilizer. Remaining emission categories are grassing animals and straw treated with ammonia. The table shows, that especially the emission from application of manure during summer and autumn has deceased during the entire period in the range 90% or more.

Table 1. Annual ammonia emissions in Denmark, where the emissions are distributed into different sectors used by the emission model (Gyldenkærne et al. 2005).

Water Test	1985 [kTon N]	1990 [kTon N]	1995 [kTon N]	2000 [kTon N]	2003 [kTon N]
Pig houses	19.787	18.674	17.979	18.578	18.578
Cattle barns	10.926	10.614	9.104	9.598	9.598
Storage	13.936	12.298	11.125	10.176	9.136
Crops	13.174	13.010	11.125	11453	11.476
Manure early spring	6.722	6.042	6.120	5.941	4.330
Manure in crops	5.491	6.680	11.296	14.183	14.129
Manure summer	8.106	7.396	3.207	1.834	512
Manure autumn	6.232	4.826	1.806	1.114	640
Manure late autumn	13.256	10.306	4.156	1.429	640
Mineral fertilizer	7.870	8.662	7.606	5.582	4.437
Grassing animals	2.591	2.413	2.500	2.370	2.257
Ammonia treatment	6.551	10.210	6.647	2.471	661
Traffic	0.053	0.106	0.993	1.828	1.989
Total	114.695	111.236	94.196	86.556	80.391

Before the year 1997, there is no detailed statistical information on farm level with geographical coordinates. However, information on agricultural areas, animal type and animal number is available on municipality level for each year. These numbers has been used to redistribute the annual ammonia emission during the period 1985-1996. Therefore, inventories for the years 1985-1996 has lower spatial accuracy than later years. However, the lower quality only affects the emission model to a very small degree as the study area applies emissions from an area of 20 km x 20 km surrounding the measuring site (Gyldenkærne et al., 2005), which is roughly twice the size of an average Danish municipality.

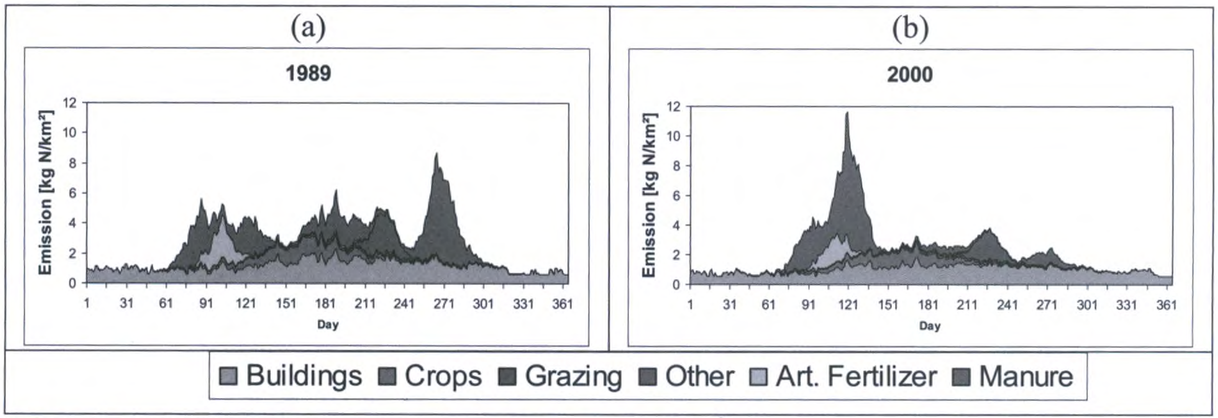

Figure 4. Calculated diurnal ammonia emission [kg N/ha²] from different agricultural sectors during the year 1990(a) and 2000 (b) for the Tange area.

Figure 4 shows an example of the calculated temporal development of the accumulated ammonia emission in the Tange area. Each color represents the sectors displayed in Table 1 generalized into 6 main groups: buildings, crops, grazing animals, other sources, artificial fertilizer and application of manure. In general the overall accumulated level has decreased from 1990 to 2003. Especially the emission resulting from the summer and autumn application of manure has decreased. Contrary the emission from the spring application has increased. Figure 5 shows the calculated relative change in monthly emission during the entire period 1989-2003 and the corresponding relative change in ammonia concentrations measured in the Tange area.

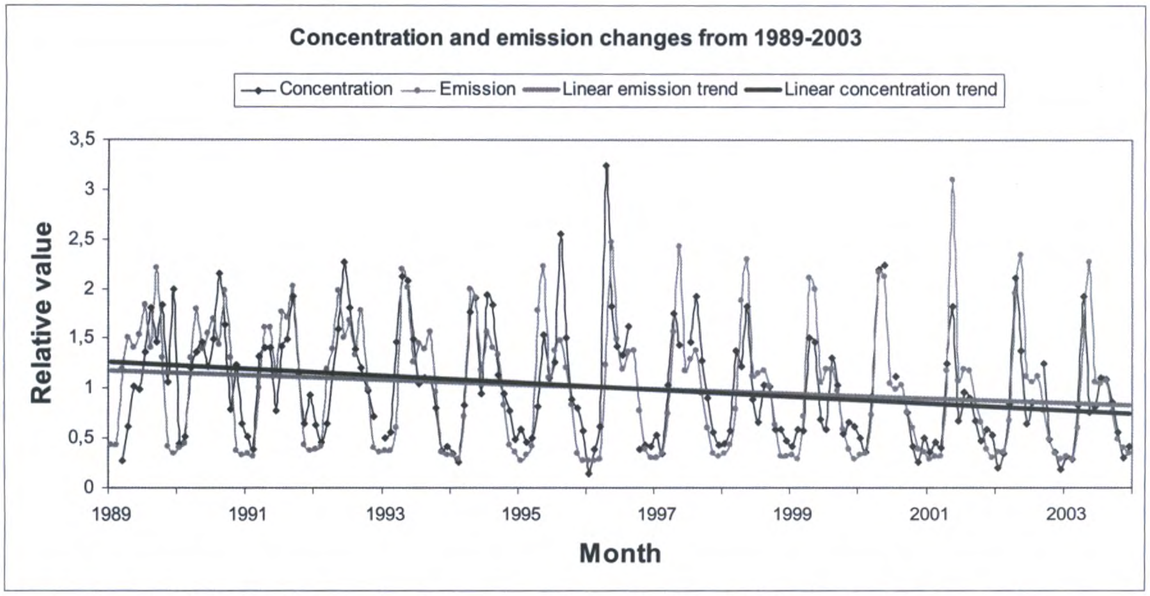

Figure 5. Calculated relative monthly ammonia emission (pink) and relative monthly ammonia concentrations (blue) for the Tange area during the period 1989-2003.

A linear trend for each time series have been applied in Figure 5. Both trends are decreasing and almost identical.

Discussion and Conclusion

A highly detailed NH_3 emission inventory based on information about the exact location of individual buildings and distribution of the number of animals within the Danish livestock has been produced for this study. The inventory has been applied by the emission model and diurnal emission calculations are performed at the measuring sites, where the results for the Tange station are discussed in detail.

For the year 1990 the emission model shows a relatively high emission level from spring to autumn (Figure 4). In 2003 several sources have been reduced significantly, where especially the contribution from manure application in the summer and autumn has been reduced (Figure 4). This decrease occurred gradually during the period 1985-2003 (Table 1). During the same period the emission from manure applied in crops during late spring have increased by more than a factor of two.

On a monthly basis a gradual change in the observed seasonal pattern of ammonia concentrations is seen (Figure 5). This change in pattern is also reflected in the results from the emission model. During the period 1989-1995 emissions as well as concentrations have shown relatively large peaks in spring and autumn. After 1995 the autumn top decreases and the spring top increases in both modeled emissions and concentration measurements.

The change in seasonal pattern (Figure 5) is a result of the Danish regulations aiming at reducing the nitrogen loss, which have forced the farmers to change general practice within the entire chain of food production. One important result is that the annual amount of nitrogen lost to the atmosphere has decreased by about one-third (Table 1 and Figure 1). Another important result is that an increasing fraction of the manure is applied during spring (Table 1 and Figure 5). Within the atmosphere, a direct consequence of the legislations is a change in the seasonal variation and a decreasing overall annual level (Figure 5).

A direct consequence of the Danish legislation is that storage requirements have increased at the same time as special demands for manure application have been enforced. Furthermore, the number of Danish farms are decreasing thus increasing the average farm size due to merging of farms. The larger farms and storage capacities decrease the number of point sources throughout the country, but increase the emission from the remaining point sources. This change increases the NH_3 gradients around the point sources and the environmental problems around these new larger ammonia hot spots. Thus care must be taken in the local regulation of the farms. This is currently being implemented with a new set of tools in the regulating of the agricultural production in Denmark. The core in the new tools is the Danish Ammonia Modeling System (Hertel et. al., 2006), which is a combination of several state-of-the-art air pollution models handling nitrogen and ammonia on local as well as regional scale.

A numerical study by Gilliand et. al (2003), showed that changing the temporal variation in NH_3 emissions over the USA changes where and when the deposition of nitrogen compounds occurs; Probably due to a seasonal differences in prevailing winds and chemical composition of the atmosphere. Therefore, applying a seasonal emission variations representing actual emission patterns probably redistributes the large scale nitrogen deposition. Therefore careful model scenarios must accompany emission reduction initiatives: These scenarios must use state-of-the-art numerical air pollution models with advanced chemical schemes and deposition modules like the EMEP (*Touvinen et al.*, 2004) model or DEHM-REGINA (*Frohn et al.*, 2002) model including the expected variations in the amount and pattern of emitted NH_3. However, the model results and measurements presented here also show, that applying significant reductions of ammonia emissions as seen in Denmark will have an immediate a similar effect on the ambient concentrations of ammonia.

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Atmospheric Emissions from a Deadstock Cremation Unit

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Abstract

The disposal of normal on-farm mortalities or deadstock is receiving more attention by both farmers and regulators alike due to issues of biosecurity and fear of recycling prion related diseases. One method for deadstock disposal is the use of small on-farm cremation units. This method is currently under review in Ontario and, as part of the review process, the environmental performance of the technology needs to be verified. As such, a commercially available, on-farm deadstock cremation unit was stack tested for various air emissions at the Arkell Research Station at the University of Guelph in September of 2005. The unit consisted of a primary chamber with a maximum rated capacity of 386 kg (850 lbs) and a secondary chamber located in line with the stack with a 0.3 second retention time. Diesel consumption for the primary and secondary burners is rated at 11.4 litres/hr (3.0 gallons/hr) and 2.5 litres/hr (0.65 gallons/hr), respectively. The stack testing protocol was designed, using established stack testing methodologies, to sample for combustion gases (O_2, CO, SO_2, and NO_X), particulate matter, acid gases, speciated metals, speciated volatile organic compounds, and speciated semi-volatile organic compounds (dioxins and furans, PAHs, PCBs, chlorobenzenes, etc.). To ascertain the level of variability in the data, tests were conducted using two different animal species (swine and poultry) with triplicate tests conducted for each animal species. This resulted in a total of six separate cremation runs being characterized for this specific unit. Results from this unit are compared to similar results from two other deadstock cremation units tested with the same protocol in 2003.

Air Quality and Emission Factors in Turkey Production

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Abstract

Airborne contaminants are factors of air quality in and emissions from the stables. Concentration of gases and particulate matter may influence health and welfare of the individuals living or working in these structures. Emissions may lead to environmental impacts. Particularly the emissions of ammonia and PM fractions must be considered in national and international emission inventories. For this purpose emission factors and activity data, for example the animal numbers, must be known.

Inside buildings, air quality is determined by monitoring the concentration of ammonia, carbon dioxide, total dust and PM10 with on-line techniques.

Emissions are investigated by measuring concentration of the contaminants and flow rates in the exhaust of forced ventilated stables. Dust concentration is measured with the gravimetric method. Fractions are calculated from an additional particle size analysis using a pre-separator, light diffraction and light scattering techniques.

The still running study is carried out in naturally and forced ventilated turkey houses. No influence of birds age, but of season and lighting procedure could be observed. In the average, concentrations remain below limit values. Total dust ranges below 4 mg/m^3, PM10 below 1 mg/m^3. Ammonia concentration normally not exceed 20 ppm.

Emissions factors depend on the age of the birds and the kind of litter. Aim of the project is to give answers to the questions of animal health and welfare, farmers health and welfare and load of the environment.

Introduction

Turkey meat becomes more and more popular and therefore consumption and production is steadily increasing. Mainly by economic reasons naturally ventilated stables are favoured in Germany but forced ventilated stables also exist. In some regions with high animal densities higher environmental loads are prevented using exhaust air cleaning techniques for forced ventilation.

In general airborne contaminants are factors of air quality in stables and environmental load by emissions from the stables. Concentration of gases and particulate matter may influence health and welfare of the individuals living or working in these structures. Emitting mass flows may lead to environmental impacts. Particularly the emissions of ammonia and PM fractions must be considered in national and international emission inventories (UN ECE 1979, 1999). Emission factors, which are required for inventories, are related to the number of animal places. Total national emissions will be calculated, compared with national ceilings and a necessity of reduction derived.

This paper gives methods and results of comprehensive investigations of the air quality in a naturally and forced ventilated turkey barn. Concentration of ammonia, carbon dioxide and total dust were measured with on-line techniques with respect to different periods of time over several periods of fattening. Dust was measured as total and PM10 fraction on-line mainly using a dust monitor. In some cases gravimetric samples were taken.

Emission measurements were carried out in the exhaust flow of the forced ventilated stables. Air flow was detected by the climate control computer which was calibrated by a grid measurement using a hot wire anemometer. Dust concentration was measured with the gravimetric method and isokinetic sampling. Fractions like PM10 could be calculated from the complete particle size distributions. Main parameters of this still running study are birds age, ambient climate conditions and different kinds of litter.

Methods and Materials

Stables

The investigations were carried out on farm level in a naturally ventilated cock house with respect to air quality inside only, figure 1, and in forced ventilated barns which belong to the experimental set-up of the FAL considering the comprehensive task.

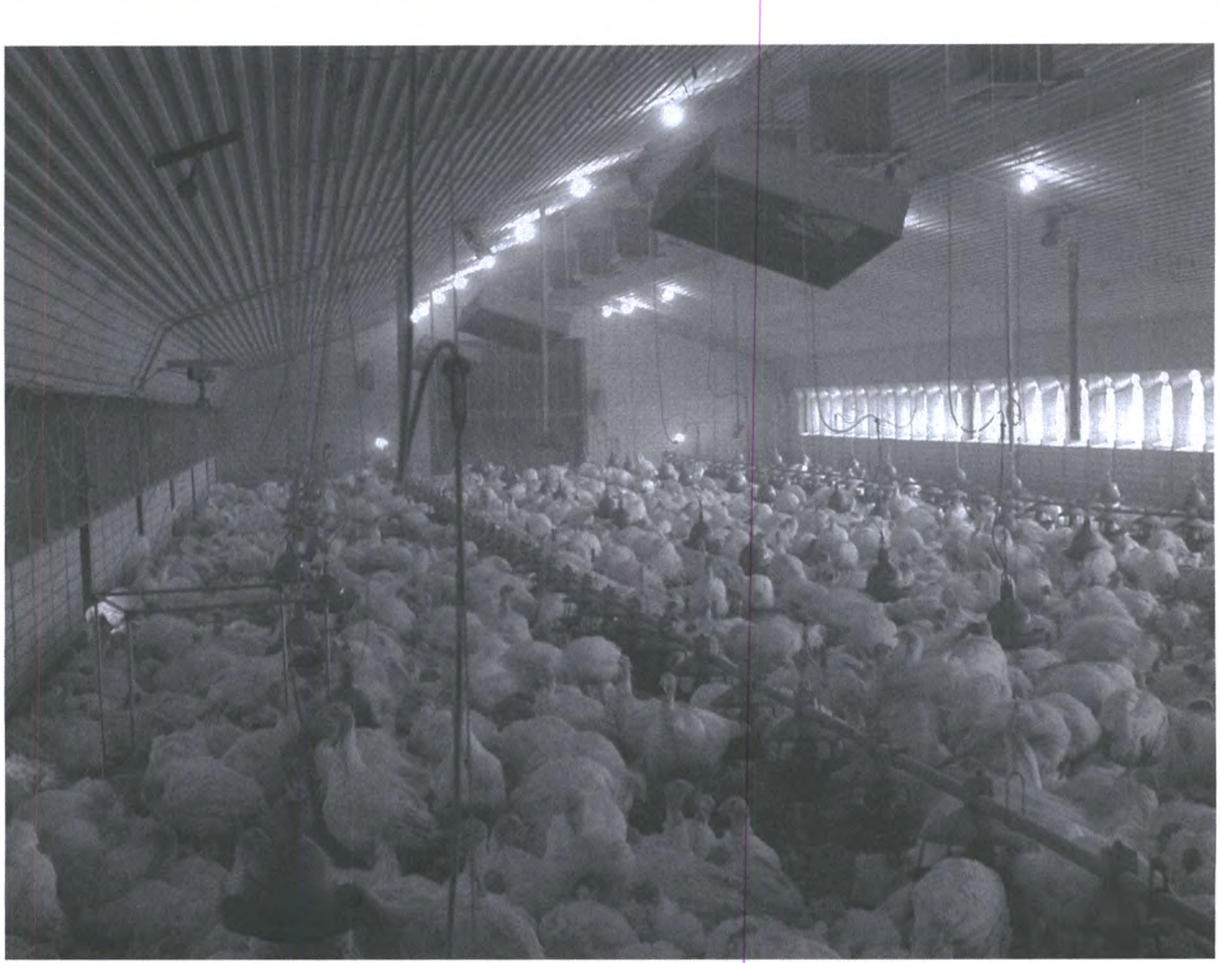

Figure 1. View into the naturally ventilated barn (Hinz et al. 2004)

The experimental set-up covers 12 single compartments as described in a former study (Hinz et al., 1999). Always two compartments form one unit with respect to the ventilation system. While in the previous study environmental enrichments for the birds were in the focus, in the present study different types of litter are investigated. A direct comparison of the results from both houses is difficult because the stocking densities were similar but not the stocking numbers.

Measuring Equipment

Concentration of NH_3 and CO_2 were measured using an opto-acoustic multi-gas monitor at one central position in each stable. Contrary to dust there are no special requirements for measuring gas concentrations in the exhaust air flow. The probes were taken in a middle area of the ducts. Flow rate was monitored by the climate control computer.

Two targets are to distinguish measuring dust and PM concentration: air quality inside with respect to human and animal health and welfare and emission flow through the outlet ducts with respect to the environment. Measurements must consider particle size fractions. Definitions e.g. from CEN, ISO and US-

EPA classify different particle fractions. They depend on effects and targets from total dust down to the ultra fines PM0.1, which were found to be hazardous to individuals and are part of global transport.

Human health-related particle size fractions according to ISO 7708 (ISO 1995) are the thoracic and the respirable (risk group) fractions. Concerning ambient air, US-EPA defined PM10 and PM2.5 (US-EPA 1987). Curves following the different definitions are given in figure 2.

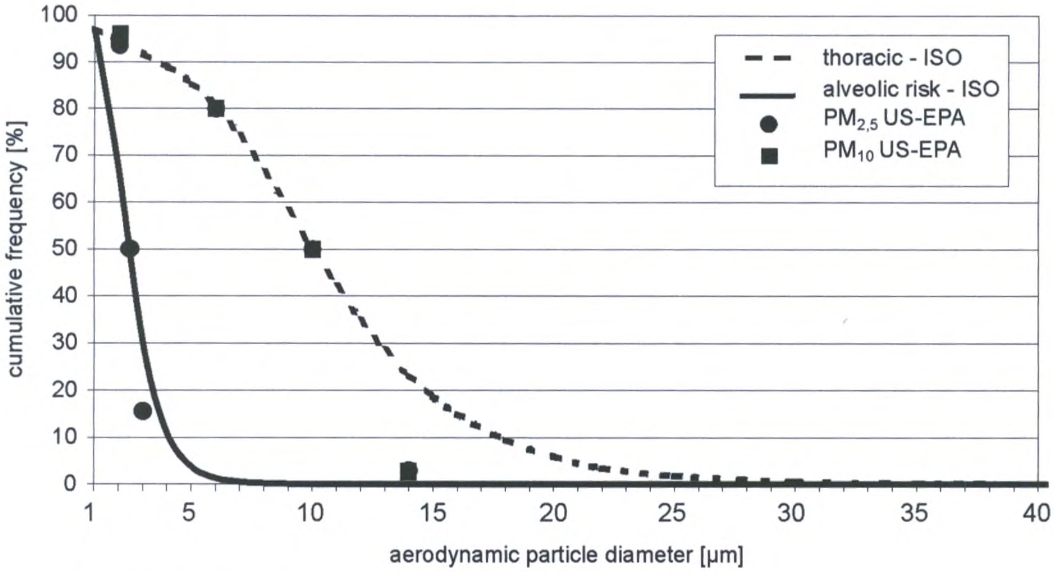

Figure 2. Fractions of PM acc. to EN ISO 7708 and US-EPA

The curves describe virtual particle separators simulating the corresponding parts of the breathing tract. They are characterized by their shape and by the 50 % value of separation and penetration. That means e.g. that 50 % of all particles with an aerodynamic diameter of 2.5 µm are alveolar while 50 % will be separated in the upper parts. The index numbers 10 and 2.5 in the US-EPA definitions mean the cut-off diameter of particle separators that the total suspended particulates (TSP) have to pass. For this particle size the separation efficiency is 50 %. In this respect PM2.5 and PM10 are comparable with the respirable (risk group) respectively the thoracic fraction but the different conventions show differences in the ranges of particle diameters concerned. Thoracic considers diameters up to 40 µm but PM10 ends at 15 µm, figure 2. PM2.5 rejects 94 % of 3 µm particles, 50 % of 2.5 µm particles and 16 % of 2 µm particles. Samplers with same cut off diameters but different shaped penetration curves will collect different fractions of PM.

TSP in ambient air means particles with settling velocities below 0.1 m/s respectively aerodynamic diameters smaller than 57 µm.

Total dust related to emission flows (often also used as TSP) may contain all sizes of dust particles up to a limit of 500 µm.

To compare results of particle concentration mearurements the used definitions must be given. The definitions above are only related to size without any consideration of substances and materials. Particle dispersions from agriculture and nature are composed by various matter of different origin. They can include inorganic matter e.g. from soil but also organic matter from plants or animals as well as dead and alive microorganism like germs, fungi, viruses, bacteria or parts of these e.g. endotoxins. The definition of these so called bio-aerosols doesn`t reflect to particle size in a specific way and will be not taken into account with the following.

Depending on the definitions and regulations particle size sensitive measurements are required. Table 1 gives possible ways for this purpose.

Table 1. Particle size-selective measurements

Aerodynamic separation	Conventional filter weighing
	Online electronic balance
	Online optical detection
Sampling total dust	Online size selective optical detection
	Conventional filter weighing with additional particle size analysis

Measurements inside the buildings followed the conditions at working site, that means all samples were collected with a sampling velocity of 1.25 m/s through a circular slot, independent from the following method of mass detection.

Inside a building the conventional gravimetric filter procedure was used as reference of total dust. The sampler was running in a high volume mode. Glass fibre filters used were pre-conditioned in a climate chamber at 20° ± 5°C and 50% ± 5% relative humidity for 24 hours before each weighing.

The TEOM instrument is mainly used for on-line monitoring of total dust. Later on a pre-separator is installed to monitor directly PM10 with a PM10 pre-separator. The heart of the TEOM is its tapered element oscillating micro balance. Particles are collected and weighed in a cumulative way. With the differences of weight in certain steps of time actual data of concentration are calculated. Averaging time depends on level of concentration. This conservative mass-related principle gives reliable results, but it must be considered that the element is heated up to 50°C. This influences the results if particles contain volatiles like VOC.

The Grimm scattered light monitor (SLM) detects the light impulses scattered by each single particle crossing the measuring volume. The instrument discriminates and counts all signals and calculates all wanted fractions from this raw data using new or previous definitions. Light intensity depends on the size, structure, the refractive number of a particle and the wavelenght of the opical source. Fig. 3 gives scattered light intensity versus particle size for a constant wavelength λ but two different refractive numbers n1 and n2.

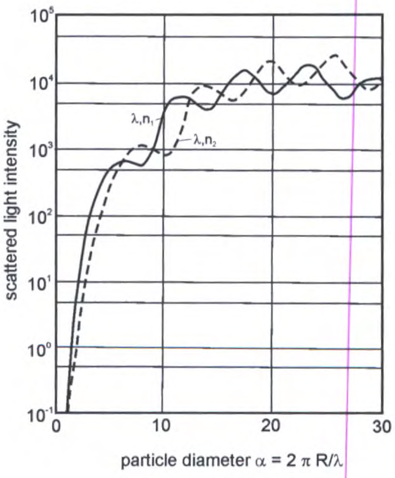

Figure 3. Scattered light intensity versus particle size for refractive numbers n1 and n2.

For this reason a calibration of the opto-electronic device is a mandatory regulation using just that material which will be measured. Otherwise an optical equivalent diameter can be given only. Fig. 3 shows this as principle limitation of such instruments for larger particles depending on n (but also on λ) no clear correlation between size and light intensity exists caused by periodical fluctuations. Most of those instruments count the number of large particles in an open upper class. With an increasing number, mass or volume information without correction becomes faulty. Hence follows that no information about TSP is available for size distributions with a high content of larger particles.

The major advantage of the instrument is its simple handling to get very quick on-line information about the influence of location or process parameters and, as mentioned above, the possible consideration of nearly all particle size definitions.

Determination of emission flows requires simultaneous measurements of air flow rate and contaminants concentration. To ensure representative samples and to avoid changes in particle size distribution by the sampling procedure itself, the so called isokinetic condition must be kept. That means equal velocities in the duct and the probe. In figure 4 the scheme of particle emission measurements in the ducts of selected compartments of the turkey house is given.

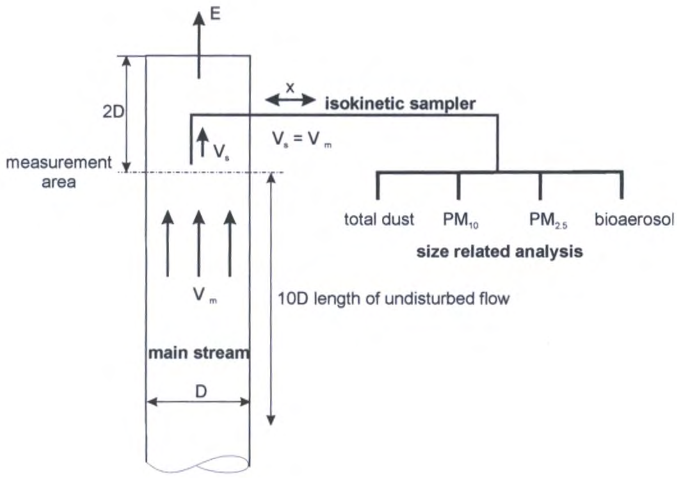

Figure 4. Scheme to measure PM emissions

A high-volume sampler with a pre-separator was used. Its fractional efficiency follows the previous fine dust definition according to the convention of Johannisburg with a cut-off diameter of 5 μm and a penetration limit for particles larger than 7.07 μm.

To get knowledge about the content of the finer particle a scattering light monitor was installed in the flow behind the cyclone separator. To determine the complete size distribution up to the largest particles the separated coarse fraction was analysed e.g. with light diffraction methods. The complete size distribution is required if PM10 or PM2.5 shall be given as percentage from total dust (TSP) as often done in the past when creating emission inventories.

Air flow was monitored as mentioned above for ammonia emissions.

Results and Discussion

Results will be presented separately for air quality inside and the emissions.

Inside the buildings, naturally and forced ventilated, for all investigated contaminants influences of the season and courses of a day could be observed. Generally the concentration is higher in winter than in summer whereby more than 90 % ranged below 20 ppm for ammonia and 4 mg/m³ for total dust. Differences were observed in the daily courses. With quite constant values over the day ammonia showed its maximum at 6am, while PM concentrations (TSP, PM10) had two peaks, one in the evening and an other in the morning. This resulted from a higher activity of the birds at that times. Concentrations were nearly constant for weekly averages. No dependency on birds age was found in the naturally ventilated barn.

Emissions were measured from the forced ventilated stable only. In the running study the birds are standing on different kinds of litter which may influence birds' health and behaviour, but also resulting emission rates.

Figure 5 shows emissions from the compartments with chopped straw and wood shaves.

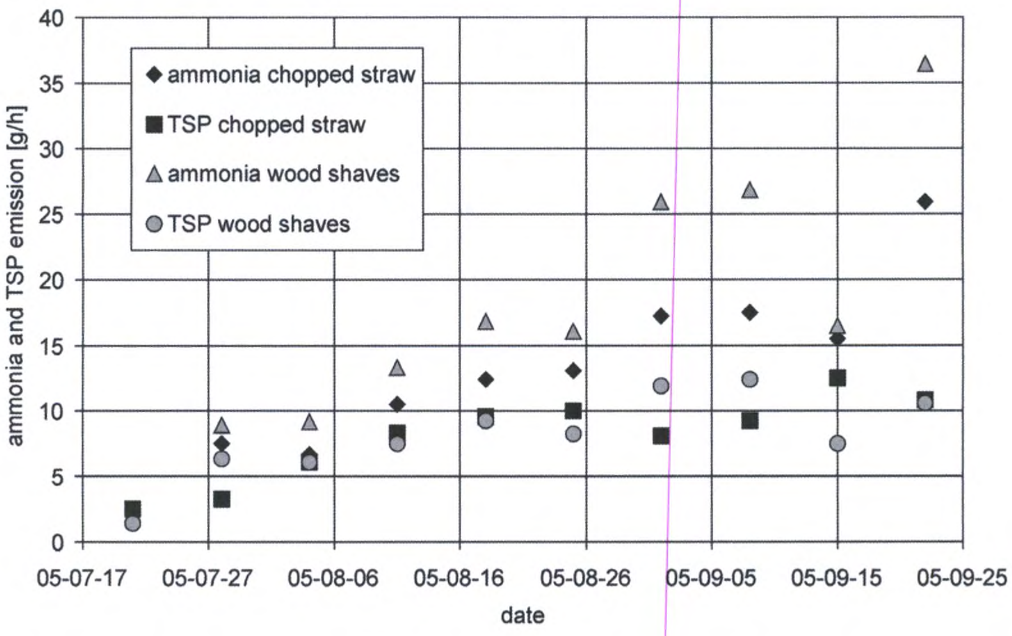

Figure 5. NH_3 and TSP emissions from turkey barns littered with chopped straw or wood shaves

An increase of emissions with birds age can be observed, but more distinct for the chopped straw and ammonia. The results reflect to animal places because the number of birds in the compartment was taken to be constant neglecting the losses. The magnitude of emissions factors and their ranges are given in table2.

Table 2. Emission factors for NH_3 and TSP

Contaminant	Emission factor [kg animal^{-1} a^{-1}]
NH_3	0.08 – 1.125
TSP	0.05 – 0.69
PM10	0.0125 – 0.17

These values are calculated on the base of 1h- averages measured in certain steps of a fattening period. They must be seen as first estimations.

Particle emissions are related to the separated fraction of the cyclone which was measured gravimetrically. This coarse fraction represented the total mass up more than 90 %. Particle size distribution of this coarse fraction showed only a small content of PM10, given for one example in figure 6. 50 % of total mass result from particles larger than 53 µm.

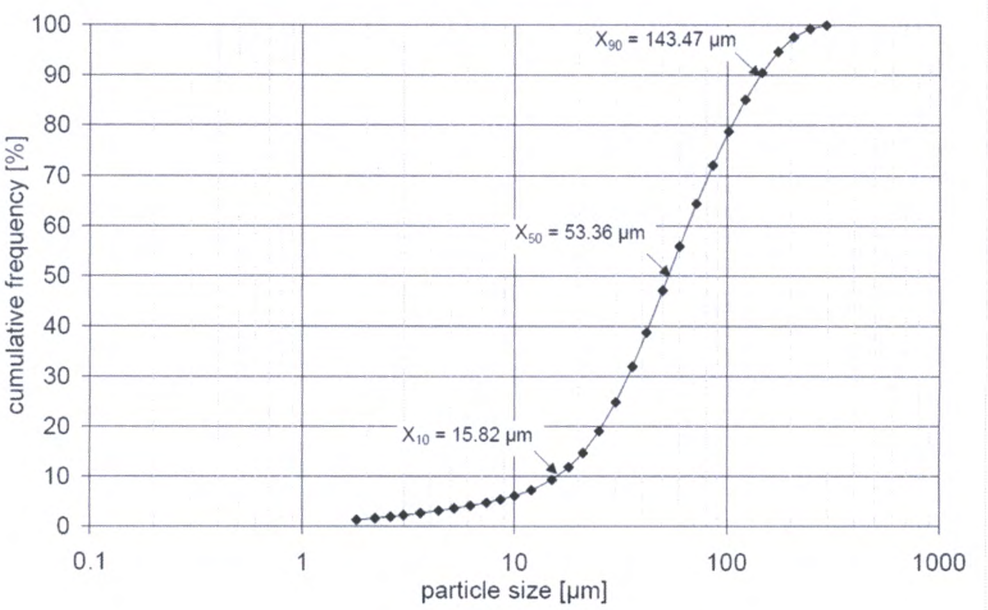

Figure 6. Particle size distribution of the TSP forming coarse fraction from the cyclone pre-separator.

Conclusions

Investigations were carried out in a naturally ventilated turkey house on farm level and in separated compartments of an experimental set-up with forced ventilation.

Concentrations of ammonia and PM were monitored inside the building with respect to farmers and animals' health and welfare.

Emissions were estimated by measuring airborne concentrations in and the air flow through the exhaust ducts of the mechanical ventilation system.

Total dust ranges below 4 mg/m³, PM10 below 1 mg/m³. Ammonia concentration normally do not exceed 20 ppm.

Emissions range between 0.08 kg animal^{-1} a^{-1} and 1.125 kg animal^{-1} a^{-1} for ammonia respectively from 0.0125 kg animal^{-1} a^{-1} to 0.17 kg animal^{-1} a^{-1} for PM10.

Particle size distribution was measured in the range of 0.5 µm up to some hundred µm particles.

Considering the conditions of the turkey houses there was no remarkable impact to farmers and animals health and welfare as well as the environment.

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Integrating Lidar and Atmospheric Boundary Layer Measurements to Determine Fluxes and Dynamics of Particulate Emissions from an Agriculture Facility

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Abstract

Lidar technology offers the ability to quantify concentrations of small particulates in the atmosphere in certain ranges of time and space. While this is a valuable tool to visualize the behavior of plumes emitted from the surface, the actual flux of particles cannot be estimated from such data alone. To determine the mass flux of particles, the concentrations must be properly integrated with wind and turbulence properties.

The goal of this study is to utilize a model that uses wind and particle density information to calculate the flux of particles from an animal facility near Ames, Iowa. The model is a simplified conservation equation for particle density in the atmosphere. This approach essentially quantifies fluxes in and out of a box centered over the facility and estimates the surface source by assuming conservation of mass.

In addition, we hypothesize that distinct turbulence structures will sometimes interact with the intermittency of the surface emission from the buildings, resulting in episodic changes in emission fluxes from the site. A second objective involves documenting how intermittent the emission plumes are and how they are connected to periodic large scale turbulence events.

Lidar data of particle size and density in the vicinity of the site were collected during an intensive field campaign lasting nearly 2 weeks. In addition to the lidar data, turbulence data were measured at several levels on each of three towers, located upwind, inside and downwind of the source area.

The model requires measurements of the vertical profiles of both concentrations of particulates and the mean horizontal wind. The concentrations were measured using the lidar, while winds were measured using a combination of cup anemometers and sonic anemometers. This allows the emission fluxes to be calculated during 15 to 30 minute periods when winds are consistent.

Flux calculations await the final calibration of the lidar returns using measured particle densities. Flux estimates will be made when distinct plumes are observed under steady-state wind conditions.

Current results are presented showing evidence of episodic plumes of CO_2 in response to intermittent vertical motions of turbulences.

Introduction

Agricultural facilities and operations result in emission of various particles and gases to the atmosphere. Among these are small particles. The emissions of small particulates from such facilities need to be quantified in order to determine the effects of such operations on air quality. Unfortunately, the size and heterogeneous nature of such facilities makes it impossible to make any simple direct measurements of emission rates.

The emergence of lidar allows measurements to be made of the spatial distribution of particles including size and density. The USU lidar was developed exactly for this purpose and allows the spatial distribution of particle density to be quantified for the atmosphere in the vicinity of an agricultural facility. However, lidar measurements of particle density will not yield the actual rate of emission from the site. This requires an integration of particle density data from the lidar with wind and turbulence information.

Determining the surface flux of particulates in this way still poses a challenge. The animal facilities especially are quite heterogeneous and variable in size. The sources have a spatially complex pattern and have distinct effects on wind and turbulence. The typical micrometeorological approaches used to estimate surface fluxes are also problematic in these cases, since they are predicated on a uniform surface or source region of adequate spatial extent.

In this case we propose using a simplified form of the conservation equation for particle density of the air to estimate the emissions for a confined animal facility near Ames, Iowa. The simplified conservation equation can be written as:

$$\frac{\partial \overline{\rho_p}}{\partial t} + \bar{u}\frac{\partial \overline{\rho_p}}{\partial x} = \frac{\partial}{\partial z}(\overline{w'\rho_p'}) \qquad (1)$$

where ρ_p is the density of particles, u is the horizontal velocity, w is the vertical velocity, t is time, and x is distance along the mean horizontal wind direction. The primes in the last term denote the instantaneous deviation of the value from the temporal mean. The last term describes the change with height of the vertical flux of particulates. In simple terms, the equation states that changes of the vertical particle flux with height are related to lateral transport or horizontal advection of particles by the mean horizontal wind. The plumes from an individual facility will only in fact rise up to a finite distance, depending upon the source strength and intensity of the turbulence. At some height z_r, the average particle density will not be affected by the local source region being studied.

Noting the above, and assuming steady-state conditions, equation (1) can be integrated to yield:

$$\int_0^{z_r} \bar{u}\frac{\partial \overline{\rho_p'}}{\partial x}\,dz = (\overline{w'\rho_p'})_{sfc} \qquad (2)$$

We now have an expression relating the flux at the surface with the horizontal changes of particle density.

$$\mathit{Surface\ Flux} \qquad \underset{0}{\overset{z_r}{\bar{u}}}\,\frac{\overline{}_{p}}{x}\,dz \qquad (3)$$

Solving this equation requires knowledge of the vertical profiles of mean horizontal wind and particle density. Essentially, equation (3) expresses the surface flux as the difference between the flux into and out of the sides of a controlled volume. Equation (3) also calculates the surface source as the difference between the lateral fluxes in and out of the control volume. A similar approach was used to estimate water vapor fluxes from irrigated patches on the landscape by Hipps and Zehr (1995) and Prueger et al. (1996).

Methods

The experiment was conducted at an animal facility near Ames, Iowa. The study was conducted in late August and early September of 2005. The animals were confined in separate buildings spaced over the site. A 20-meter tower was located in the middle of the facility, and there were 7-meter towers both upwind and downwind of the site. Measurements were made at three heights on the large tower and two heights on the smaller towers. At each location, high frequency measurements of 3-dimensional wind, air temperature, water vapor density, and CO_2 density were made. All measurements were made at 10 Hz. The 3-D sonic anemometer (Model CSAT3 – CSI, Logan, UT) was used for measurements of wind and temperature, while the LiCor Model 7500 was used to measure water and CO_2 densities. In addition, a vertical array of cup anemometers was mounted on each 7-meter tower.

The lidar and other air quality measurements during this experiment are described elsewhere in these workshop proceedings. These measurements allow the actual particle density at certain size ranges to be computed for each spatial element mapped by the lidar.

The first step is to document periods when plumes were observed and the lidar was scanning in an appropriate pattern to measure the upwind and downwind faces of the control volume. The setup and a conceptual picture of this approach are depicted in Figure 1.

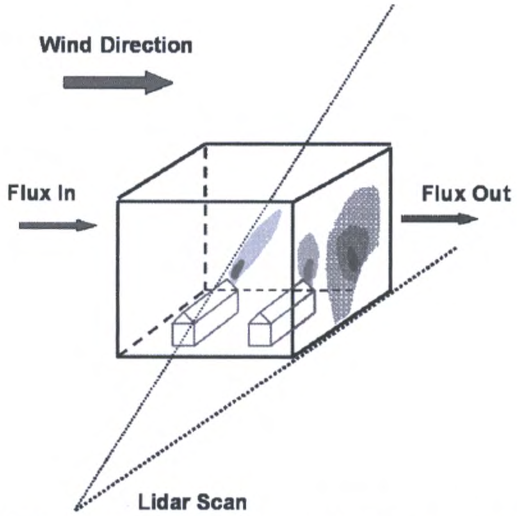

Figure 1. Representation of the approach used to calculate surface emissions.

When distinct plumes of emission were observed during fairly steady-state conditions, the wind and lidar data can be input into equation (3) to solve for the average surface emission. These calculations will be completed for all periods during the experiment that meet the above criteria.

Periods will be identified when distinct turbulence structures are present and related to fluctuations in plume activities. The intermittent nature of both the turbulence and emission will be conducted by examining the time series of turbulence data and plume behavior as measured by the lidar.

Preliminary Results

Currently the lidar data are being calibrated to measured particle concentrations to produce images with actual density units. These must be produced before the flux calculations can be made. However, the turbulence measurements of vertical wind and CO_2 density can be used to look at some of the intermittent behavior of CO_2 from the facility.

Some connections between episodic turbulence structures and emission can be observed by looking at the vertical wind and CO_2 density time series. Figure 2 illustrates a case in which there is a strong coherence between large updrafts of vertical wind and CO_2 density at the 12-meter level on the tower in the middle of the complex. There are about 15 minutes of data plotted.

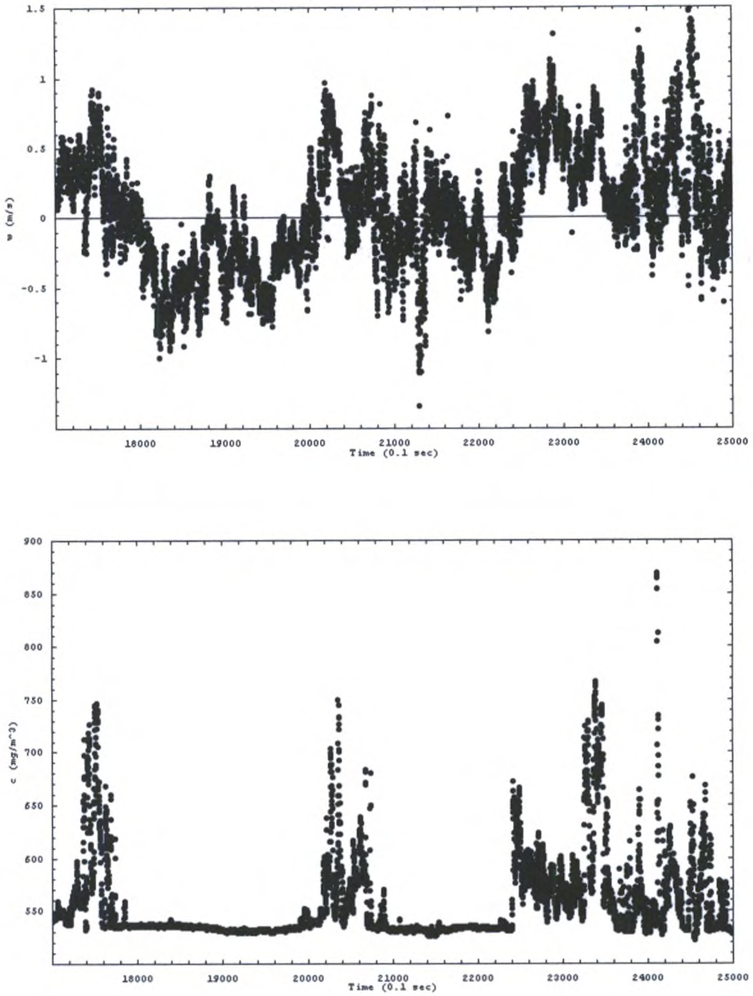

Figure 2. Time series of vertical velocity and CO_2 density at a height of 12 meters above sources.

The data are from a period in the morning when convection was just starting to couple the lowest surface layer with the air above. Note that the CO_2 remains near constant during periods of either weak vertical motion or downward vertical gusts. The source of the CO_2 is the buildings below, and under these conditions, it does not reach the sensor. However, periodically strong updrafts associated with passage of a large eddy bring up plumes of larger CO_2 density.

Future analyses will examine the coherence between plume emissions and transport with distinct turbulence events and structures. This will indicate how emissions are affected by periodic large scale eddies sweeping the source area. The implications for modeling the transport of particulates will be addressed.

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Quantifying Aerosol Mass Remotely from Real-Time Lidar Measurements

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Abstract

The purpose of this project was to develop a technique to measure remotely in real-time, aerosol mass emitted from agricultural operations. Lidar measurements of plumes emitted from field preparation and spray operations are used as examples of the technique. This paper demonstrates the integration of lidar images of aerosol plume cross sections to determine suspended concentrations. These integrations are combined with aerosol size distributions to determine the volume distribution of aerosols in the plume over time.

Introduction

Agricultural operations act as aerosol sources in a variety of ways. Two such sources are aerial spraying and field preparation (figure 1). To date, little is known about the dynamic concentrations, fluxes and transport distances of such aerosols (Holmén et al. 1998). Aerosol plume characteristics, such as concentration, are typically predicted via models such as AgDrift (Teske et al. 2002). Traditional methods of measuring non-point source aerosols are via samplers in the field (Clausnitzer and Singer 1996) or downwind (Hoffmann and Kirk 2005) which are only useful for small areas or spatially regular plumes. In an effort to overcome these limitations remote lidar measurements of agricultural plumes have been combined with traditional point sampling to measure the extent of plume movement and concentration across the plume area (Holmén et al. 2001a; Holmén et al. 2001b). This work presents a new calibration technique that allows the remote measurement of plume concentration via lidar. It shows results of the calibration from both an aerial spraying operation and a traditional cotton field preparation operation. Both studies took place near Las Cruces, New Mexico in the spring of 2005.

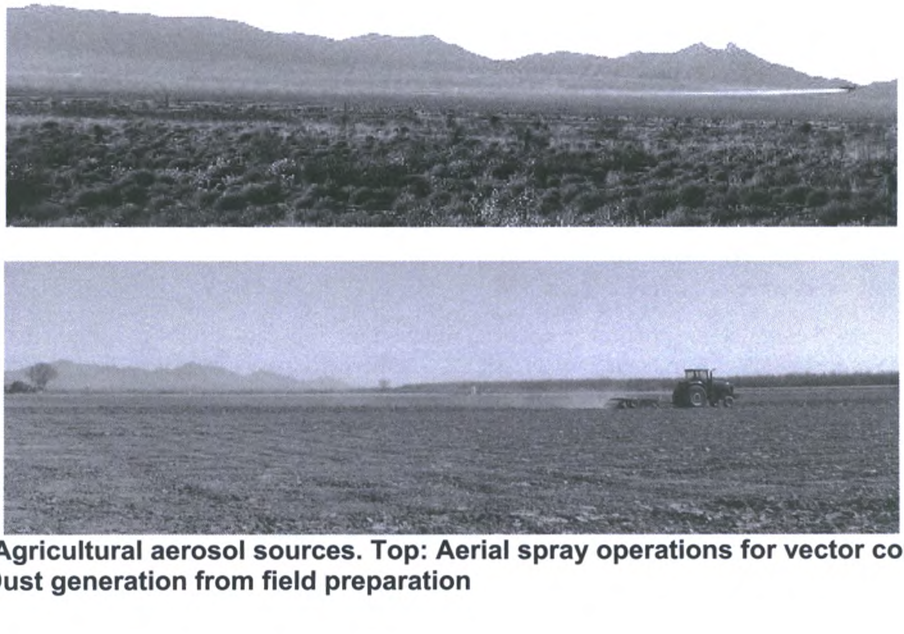

Figure 1. Agricultural aerosol sources. Top: Aerial spray operations for vector control, Bottom: Dust generation from field preparation

Methods

Measurements

Near dawn on April 27, 2005, the New Mexico State University Cessna T188C aircraft applied oil based tracer in five single-pass swaths to simulate vector control operations. Each pass of the aircraft was monitored remotely by the University of Connecticut elastic backscatter lidar. The lidar is capable of taking cross sectional measurements of the relative plume concentrations by slicing through the plume vertically.

Traditional farming practices for cotton were performed at the New Mexico State University Leyendecker Plant Science Research Center. The lidar was used to measure the particle concentration above the field as generated from the farming operations. In this study, the lidar took horizontal scans across the field at several different heights. This results in a three dimensional volume image of the plume. Figures 2 and 3 show a representative area and volume lidar images of the spray plume and dust plume respectively

Particle size distributions for the aerial spray were determined from wind tunnel calibrations of the spray nozzle configuration. Emission rates were the application rate for a unit length of aircraft movement. Particle size distributions of dust from the field operations were determined by sampling with cascade impactors and real-time mass monitors. Emission rate was determined from the maximum sampling measurement adjusted for unit length of tractor movement.

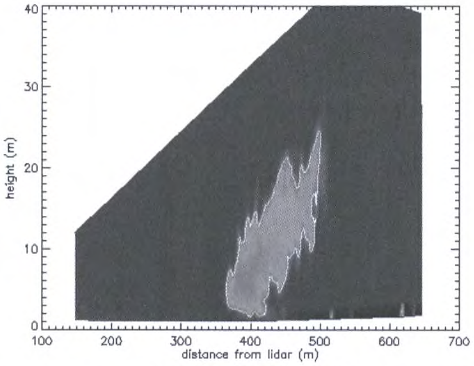

Figure 2: Representative cross sectional slice of aerial spray plume

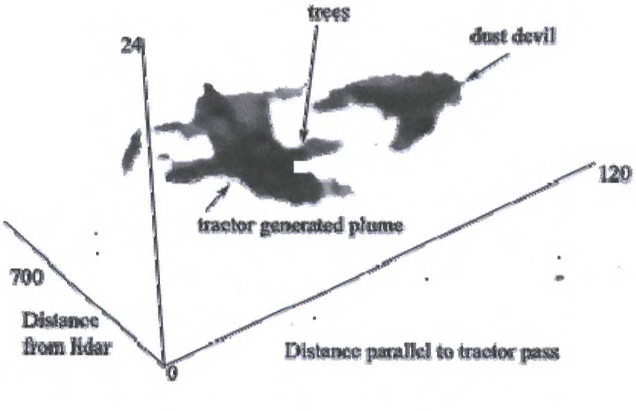

Figure 3: Lidar volume from one pass of the tractor. The reconstructed volume shows a line of tress behind the field, the dust generated from the tractor operation and a dust devil that occurred during the scan. Distance units are relative lidar units.

Determining Concentration

The technique to determine concentration consists of two steps. First the measured particle size distributions and emission rates of a test plume are used to calculate predicted plume concentration. Second, a conversion factor for lidar backscatter to concentration is found by finding the linear relationship between the predicted concentration and the total measured backscatter in the plume volume. This conversion factor is then used to convert the lidar measurements to concentrations across the plume. Figure 4 presents the relationship used to find the conversion factor for the airplane spray study. Figure 5 shows an example of the resulting spray plume concentration dynamics.

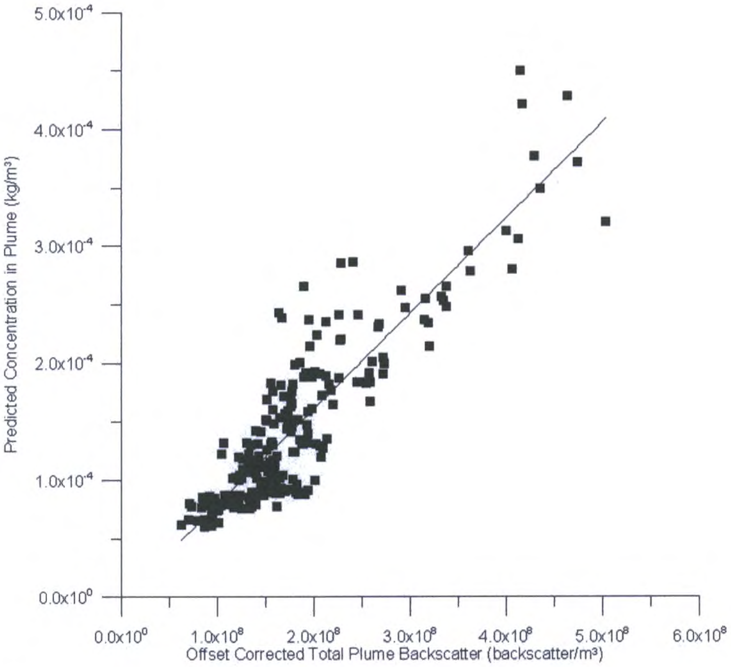

Figure 4: Predicted plume concentration vs. total lidar backscatter for three pass of the airplane. The linear relationship has a slope of 8.18e-13, which is used as a conversion factor between lidar backscatter and aerosol concentration.

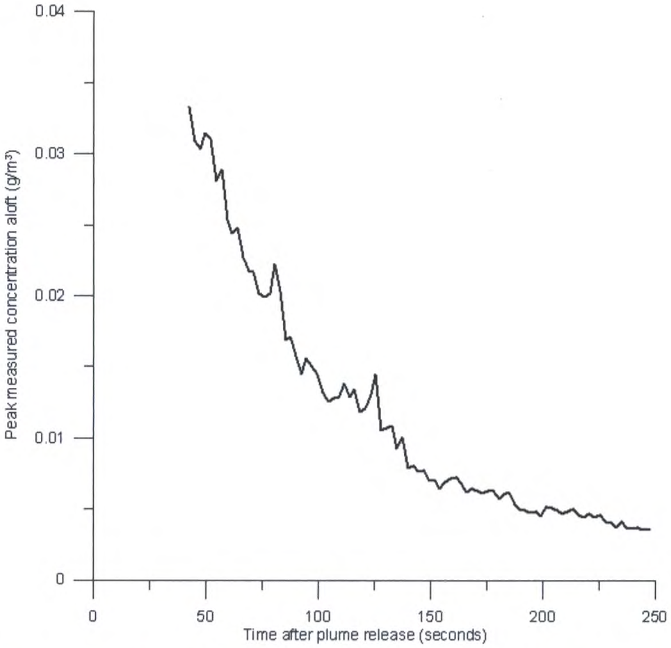

Figure 5: Remotely measured peak concentration in the plume after release for a single pass of the airplane.

Conclusions

It is possible to remotely measure the concentration of aerosol plumes in the air. Lidar offers a usable technique to perform such measurements and a viable technology for studying agricultural air quality.

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Biofiltration of the Critical Minimum Ventilation Exhaust Air

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Abstract

This research project investigated the gas and odor emission reduction potential from a deep-pit swine finisher using a strategy of partial biofiltration of a critical minimum amount of exhausted air (CMEA). The CMEA was defined as the amount of air exhausted to a stable hot-weather atmosphere, typical of summer night conditions. Ventilation air exhausted during the heat of summer days is exhausted into an atmosphere that is, for the vast majority of times, very unstable providing excellent natural mixing potential near the building source. In more stable evening atmospheres, biofiltration of the CMEA would reduce gas and odor emissions and the potential for odor plumes to travel long distances. The overall effect could be a more attractive and affordable biofiltration strategy that maximizes odor and gas reduction potential when it is needed most.

For this research project the CMEA was fixed at 75 m^3-h^{-1}-pig^{-1}. The preliminary results from this on-going research effort indicate an ammonia reduction of the pit-exhaust air of 44 percent, a hydrogen sulfide reduction of 58 percent, and an odor reduction of 54 percent.

Introduction

Odor and gas dispersion from swine facilities is receiving much attention. Sources of odor and gas emissions include land application events, manure storage facilities, and building exhaust air. Ventilation air is typically exhausted into the ambient atmosphere without treatment. This exhaust air contains odorous gases and particulate matter that can represent a concentrated odor source.

Many researchers have examined odors from livestock facilities to determine the constituents that are most influential in olfactory perceptions. Hammond *et al.* (1979) found that the most important compounds were acids, phenols and carbonyls. However, results indicated that odors occurring at large distances from animal facilities were amplified by the presence of dust particles (Cai *et al.*, 2005). Hartung (1985) stated that filtering the dust from exhaust air can reduce the odor emission from animal houses up to 65 percent.

Biofiltration works well for treating odors and contaminated gases from livestock sources because an uncharacterized population of microorganisms can adapt to the profile of compounds to be treated. By-products are primarily water, CO_2, mineral salts, and oxidizable inorganic compounds. Biofilters have been shown to remove in excess of 90 percent of the odor, 95 percent of the hydrogen, and 60-75 percent of the ammonia emissions from a livestock source. Thus, biofiltration is an effective technology to improve air quality adjacent to and downwind from livestock facilities. Biofilters are relatively economical and simple to install and maintain, but require a large land area and in most designs require higher capacity fans to move the ventilation air to be treated through the filter material.

Noren (1985) used peat and heather over wooden slats to form a biofilter for animal housing. It was found that odors were absorbed and converted by microorganisms to odorless substances after the biofilter was allowed to mature. Gases were decreased at an average rate of 50 percent with an 80 percent removal rate when the biofilter was kept at an optimal moisture content. Zeisiz and Munchen (1987) used several different materials including humus soil, compost, and peat. O'Neill and Stewart (1985) summarized the effectiveness of biofilters showing the odor removal efficiency ranged from 50 to 90 percent. Biofiltration adapted to U.S. animal production practices has been studied in detail with specific design guidelines given by Nicolai *et al.* (2002), Janni *et al.* (2001) and Nicolai and Janni (2001).

For this research project, the objective was to define and treat *via* biofiltration the least amount of ventilation air possible. This air, called the critical minimum exhaust air (CMEA), was defined as the amount of exhaust air that resulted in the most potential for downwind odor complaints by near-by residences. The objectives of this research project were to;

1). Determine and propose the CMEA for a typical deep-pit swine finishing facility,

2). Modify an existing deep-pit swine finisher to biofilter the CMEA, and,

3). Monitor concentrations of hydrogen sulfide, ammonia, and odor from a CMEA biofiltered barn compare with a conventional pit-ventilated deep-pit swine finisher.

Methods

Determining the Critical Minimum Exhaust Air (CMEA)

A six-state research project funded by the USDA-IFAFS program (APECAB) was conducted to investigate gas and particulate emissions from swine and poultry facilities. This project measured real-time emissions from fan ventilated animal and poultry housing facilities. A critical variable measured during this project was the real-time airflow rates required to assess gas and particulate emissions. In Iowa, a deep-pit swine finisher was monitored. The airflow data collected in Iowa showed that even in the heat of the summer, the evenings cooled enough forcing the barn to ventilate at a rate that was about 50 percent of the maximum mid-day requirements. A typical two-day result for August 2003 is given in Figure 1. The amount of ventilation air exhausted between day and night time periods is being delivered to two very distinct atmospheres. During hot summer days, the air is being exhausted to a predominantly unstable environment where very good natural vertical mixing of the exhausted air with fresh ambient air is being realized near the source. During the evening periods, the air is being exhausted into a relatively stable atmosphere, implying that natural vertical mixing is low and the potential for ground-level gas concentrations at further downwind distances is more probable than during the heat of the day. It is not uncommon for the ventilation rate to change from 35 fresh-air-changes per hour (ACH) during the night to a maximum of 100 ACH during the heat of the day. To biofilter all ventilation air (i.e. 100 ACH) would not be practical, and, based on atmospheric stability conditions is unwarranted. This change in ventilation requirements, as a function of atmospheric stability, can be used as an advantage with respect to ventilation air mitigation using biofilters or any other ventilation air mitigation strategy in general.

During the cooler and more stable evening hours, odors and gases exhausted from buildings have the potential to travel greater distances than those exhausted during the unstable daytime hours. Therefore, it makes practical sense to treat the night-time ventilation air to offset the lack of natural atmospheric mixing present during the heat of the day. This night-time exhausted air was defined for this research project as the CMEA. For this research project, the CMEA was defined as the amount of air associated with a rate equal to 75 m^3-h^{-1}-pig^{-1}. For the barn shown in Figure 1, with a capacity of 960 pigs, corresponds to a CMEA treatment level of 72,000 m^3-h^{-1}.

Barn Changes Made to Accommodate the CMEA

Two side-by-side 300-hd deep-pit swine finishing rooms were used at a cooperator's site in central Iowa (Figure 2). The control room was left unaffected and consisted of two 61-cm diameter variable speed fans drawing air from the head-space of the manure pit, exhausted directly to atmosphere. The balance of ventilation air was provided with side-wall curtains. The test room, originally identical to the control room, was modified in the following ways to accommodate the biofiltration of the CMEA:

a. The two 61-cm diameter pit fans as shown in the control room were removed and replaced with four single-speed fans, two each in two separate exhaust plenums (Figure 2).

b. A biofilter consisting of wood chips was installed at a depth of 27 cm and a surface area of 80 m^2.

The installed biofilter fans, labeled as shown in Figure 2, were controlled in four stages with the characteristics given in Table 1.

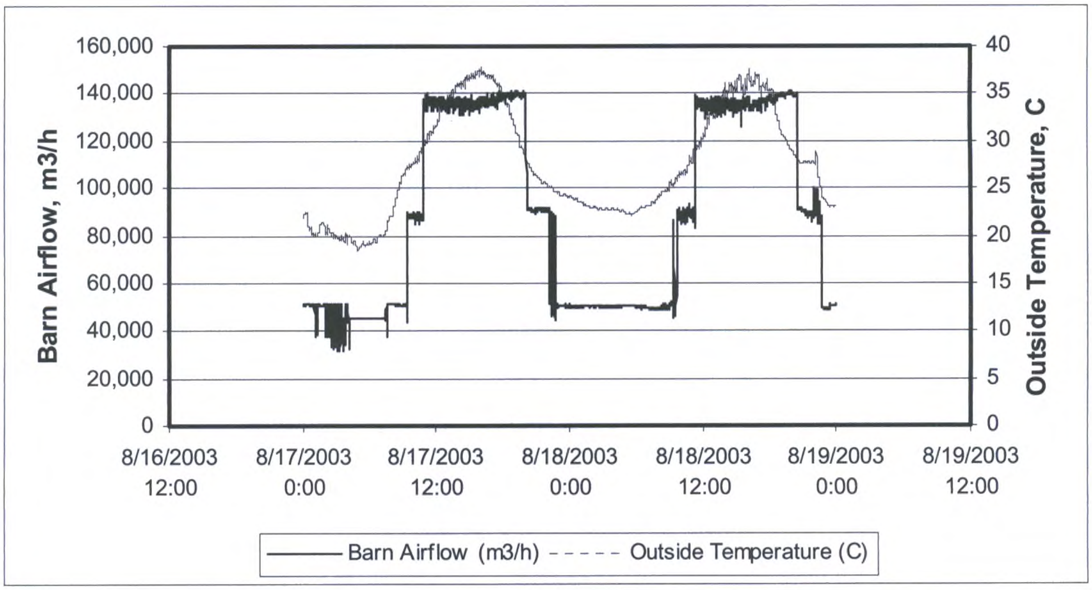

Figure 1. Building airflow changes with summer outside temperature.

Table 1. Fan staging to achieve the CMEA requirement .

Fan Stage	Fans Active*	Measured Operating Static Pressure (Pascals)	Estimated Airflow** (m^3-h^{-1}-pig^{-1})
1	1	13	6
2	1 and 2	13	18
3	1 and 2 and 3	37	49
4	1 and 2 and 3 and 4	50	77

* Fan 1=30-cm diameter, Fan 2=41-cm, Fans 3 and 4=61-cm

** based on 85% of rated capacity at the operating pressures measured for each stage

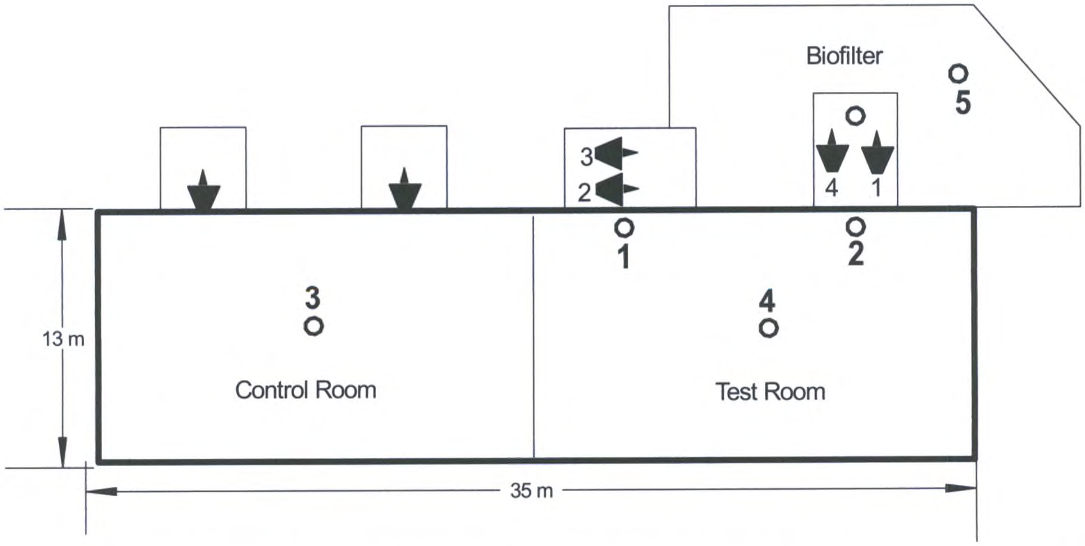

Figure 2. Building layout showing control and test room set-up with sampling locations (SL).

Gas Concentration Sampling

A Mobile Emissions Laboratory (MEL) was installed on-site that housed all monitoring equipment. Ammonia and hydrogen sulfide sampling was conducted semi-continuously with odor sampling conducted bi-weekly. Ammonia and hydrogen sulfide were monitored using a chemiluminescence-based analyzer (TEI, Inc; Model 17C) with hydrogen sulfide monitored using a pulsed-fluorescence-based analyzer (TEI, Inc; Model 45C). Gas samples (see Figure 2) were routed through 10-mm ID Teflon-lined sample lines to a common sampling system with switching solenoids to route samples at each location, in sequence, to the NH_3 and H_2S analyzers. All sample lines were heated at critical locations where condensation could occur and each sample line was fitted with a 0.45-µm particulate filter at the intake. Samples from each sample location were presented to the analyzers for a total of 10-min with the final 4-min of each sampling sequence used for analysis. Odor samples were collected from each sampling location, collected in 10-L Tedlar sample bags and evaluated using dynamic dilution olfactometry (St. Croix Sensory, Inc; Model AC'SCENT).

Results and Discussion

Ammonia, Hydrogen Sulfide and Odor Concentration Results

Gas and odor concentrations were collected between July and October 2005 with the results shown in Table 2. Odor concentration entering the biofilter plenum from the head-space of the deep-pit (sample lines 1&2) averaged 1,169±788 OU/m^3 with an average odor concentration leaving the biofilter (SL=5) of 540±316 OU/m^3. These differences represented an average reduction in odor concentration of 54 percent ($p<0.01$). The control barn room air (SL=3) odor concentration (603±484 OU/m^3) compared with the test room air (SL=4; 577±546 OU/m^3) was not significant ($p>0.50$) and the biofilter exhaust air (SL=5) was not significantly different ($p>0.50$) from the biofilter room air (SL=4). The ammonia concentration entering the biofilter plenum from the head-space of the deep-pit (SL=1) averaged 9.1±5.5 ppm with an average ammonia concentration leaving the biofilter (SL=5) of 5.1±3.4 ppm. These differences represented an average reduction in ammonia concentration of 44 percent ($p<0.01$). The control barn room air (SL=3) ammonia concentration compared with the test room air (SL=4) was not significant ($p>0.50$) and the biofilter exhaust air (SL=5) was not significantly different ($p>0.10$) from the biofilter room air (SL=4). Similar results were found for hydrogen sulfide.

Table 2. Average (±SD) odor, ammonia and hydrogen sulfide concentrations measured between July and October 2005 for the sample locations shown in Figure 2.

Sample Location (SL)	Sample Descriptor	Odor Concentration (OU/m^3)	Ammonia Concentration (ppm)	Hydrogen Sulfide Concentration (ppb)
1 & 2	Pit Exhaust	1,169±788	9.1±5.5	253±263
3	Control Room	603±484	3.7±3.2	95±94
4	Test Room	577±546	3.6±3.1	90±113
5	Biofilter Exhaust	540±316	5.1±3.4	106±104

Assessment of Gas Emission Reduction Using Biofiltration of the CMEA

The odor, ammonia and hydrogen sulfide reductions reported here using the installed biofilter were modest. The biofilter installed was developed in such a way that fan pressure drop was a key variable used in an attempt to develop a biofilter that could be used with existing agricultural fans. For this design constraint to be realized, the decision was made to develop a biofilter that resulted in no more than a 60 Pascal pressure difference. The end result, after several iterations, was a biofilter consisting entirely of wood chips. Also, in order to achieve the reductions presented here, the biofilter media had to be frequently wetted to prevent drying of the material.

Conclusions

This on-going research on biofilter technology applied to fan ventilated animal housing facilities concentrated on the biofiltration of the critical minimum exhaust air (CMEA). This was defined as the amount of ventilation air required by swine finishing facilities during night-time summer periods. For this research project the CMEA was fixed at 75 m^3-h^{-1}-pig^{-1}. The preliminary results indicate an ammonia reduction of the pit-exhaust air of 44 percent, a hydrogen sulfide reduction of 58 percent, and an odor reduction of 54 percent. Further research will be conducted on biofilter additives to improve gas reduction efficiencies without increasing back-pressure on the exhaust fans. The authors would like to thank the Iowa Pork Producers Association and the USDA-Special Grants program for funding this on-going research.

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A Novel Rapid Method for the Characterization and Identification of Aerosols: Multi-Elemental Scanning Thermal Analysis (MESTA)

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Abstract

A rapid and sensitive method for the chemical analysis of aerosols is highly desirable for air-quality monitoring and research works. Here, I report the application of a newly developed multi-elemental scanning thermal analysis (MESTA) for chemical analysis of aerosols. We collected $PM_{2.5}$ samples from the university campus (city) and from the Experimental Station (rural) and analyzed them with the MESTA. The results indicate that the $PM_{2.5}$ campus and the that of the Experimental Station were different in the relatively low C/N/S ratio in the campus when compared to the rural Station. The $PM_{2.5}$ collected near the pig pan of the Quincy Station, however, show similarity in chemical signature to that found in the campus. The weekend campus samples were similar to the weekday samples in chemical signature although the $PM_{2.5}$ concentration was slightly higher during the weekends. In addition to the bulk chemical information, the MESTA reveals chemical signature of the $PM_{2.5}$ components. Results of this study suggest that the MESTA technology could be a rapid and effective way to study aerosols in the air.

Introduction

A rapid and sensitively method for the chemical analysis of aerosols is highly desirable for air-quality monitoring and research works. Unfortunately, such basic requirement is still not met currently due to the limited separation techniques developed for solid samples. Traditional sequential extraction technique is not only tedious and incomplete, it may introduce contaminants and artifacts to an aerosol sample. Bulk elemental analysis can provide some chemical information but it is generally insufficient for identification and characterization purposes. Besides technical problem in separation, aerosol analysis requires high sensitivity and speed due to small size and possible post-sampling change of a sample. Various carbon scanning thermal analysis techniques have been developed to examine particulate air samples in the last two decades (Chow *et al.* 2001). In addition to the information of carbon content, carbon scanning thermal analysis also reveals about the temperature at which the carbon volatilizes (i.e., a carbon thermogram). Carbon scanning thermal has been quite efficient for differentiating different forms of carbon compounds in a solid sample. For example, organic, elemental and carbonate forms of carbon can be readily differentiated by their characteristic volatile temperatures in a carbon scanning thermal analysis(Conny *et al.* 2003). Carbon scanning thermal analysis reveals only the carbon information. Important information such as nitrogen and sulfur in aerosol is not available from carbon scanning thermal analysis. Here, I report the development of a multi-elemental scanning thermal analysis (MESTA) that can quickly and sensitively analyze aerosol samples and provide the information on C, N and S simultaneously. The simultaneous C, N and S thermograms of the MESTA provide chemical signature of organic and inorganic components in an aerosol sample. We demonstrate the application of MESTA to $PM_{2.5}$ collected from the air of the campus and a rural Quincy Experimental Station. The simplicity, reproducibility and sensitivity of MESTA make the technology a good tool for air quality research.

Materials and Methods

The MESTA device

A prototype MESTA system has a quartz pyrotube that consists of a sample compartment and a combustion compartment. The combustion compartment is maintained at 1100 °C by a constant-temperature furnace. The sample compartment can be heated to 800 °C from ambient temperature at a given rate through a programmable furnace. The sample compartment has a gas inlet for carrier gas, a mixture of oxygen and helium. The mixing ratio of helium and oxygen in the carrier gas is adjustable by two flow meters. The combustion compartment has an inlet for pure oxygen. The pyrotube is connected to detectors of C (a CO_2-IR analyzer), N (a NO_2 chemiluminescent detector) and S (a SO_2 chemiluminescent detector) in a serial manner. A PC based four-channel data logger (National Instrument) is used to record simultaneously the real-time temperature, C, N and S signals. When an analysis is performed, a weighed sample (0.1 – 20 mg) is loaded into a quartz boat and then inserted into the sample compartment. The sample compartment is then closed with a Teflon plug. After the air is purged out of the pyrotube by the carrier gas, the sample compartment is heated at a constant rate (50 °C/min) from ambient to 800 °C. As the temperature of the sample compartment increases, volatilized component of the sample is carried to the combustion compartment with carrier gas where C, N and S are oxidized to their respective oxides. The combusted gas stream is dehydrated and purified with filters and the oxidized C, N and S gases are detected by the respective detectors. The result of the analysis is displayed as C, N and S thermograms. Silver sulfide (Ag_2S) and elemental sulfur (S_8) are used as temperature markers to calibrate the thermograms as desired.

Ambient Air Sampling

Weekday and weekend air samples were collected from the Florida A&M University campus (Tallahassee, FL) on the rooftop of a 6-story building that was located approximately 600 meters from a main road intersection. Air samples were also collected from the Quincy Experimental Station of the Florida A&M University at two sites: one close (10 m) to the pig pan area and the other close to the office area, which is 300 m from the pig pan. $PM_{2.5}$ samples were collected using a $PM_{2.5}$ air sampling device that had been designated by EPA as Equivalent using the VSCC (Designation No. EQPM-0202-142; Model PQ200; BGI, Inc.) and with a pumping rate of 16.7 liters per minute. The PM2.5 was collected on a pre-weighed and pre-fired (900 °C, 2 h.) 47 mm quartz filter inside the sampler. Total sampling collection time ranged from 27 to 60 hrs. After the set sampling time, the filter was removed and weighed again and the $PM_{2.5}$ concentration was calculated based on the filter weight difference and the total volume of air that passed through the air sampler. Each collected filter was put in a pre-fired stainless steel container and stored in a freezer until analysis. The weekday samples represent cumulative samples that were collected between 11 am and 6 pm each day for five days. The weekend air sample was collected for approximately 40 hours continuously during the weekends.

PM Sample Analysis

The quartz filter that contained the $PM_{2.5}$ sample was weighed and cut into eight pie-shaped pieces. Each piece was weighed. The piece/total weight ratio was used to calculate the portion of the PM sample in that piece. A piece of the filter was loaded in the sample holder and the MESTA was carried out from 35 to 800 °C with 50 °C/min heating rate, 40 % oxygen 60 % helium carrier gas. The C, N and S thermograms of MESTA were recorded using a data logger (National Instrument). The C, N and S signals in the thermograms were calibrated to their relative atomic abundance with pure cystine standard.

Results and Discussion

The $PM_{2.5}$ concentration and its chemical property of the air samples are listed in Table 1. The $PM_{2.5}$ in the ambient air of the Tallahassee campus was significantly higher than that in the Quincy Experimental Station near the office area. The highest $PM_{2.5}$ observed, however, was in the air close to the pig pan of the Quincy Station: about three times the $PM_{2.5}$ concentration of the office area just 300 m away.

The $PM_{2.5}$ in the campus during the weekends was slightly higher than that during the weekdays for some unknown reasons. The most noticeable is the higher nitrogen and sulfur contents relative to the carbon found in the impacted areas associated with higher $PM_{2.5}$ concentration. For example, the campus $PM_{2.5}$ during the weekdays had average C/N/S ratio of 5.9/1.7/1. The C/N/S ratio of the campus $PM_{2.5}$ became 4.3/1.6/1 during the weekends when the $PM_{2.5}$ was slightly higher. The $PM_{2.5}$ concentration of the Quincy Station was lower than that in the campus. But the $PM_{2.5}$ C/N/S ratio is much higher at 36.1/7.3/1. The impacted Quincy Experimental Station air near the pig pan area showed a distinct $PM_{2.5}$ C/N/S ratio of 3.1/2.8/1. The above results indicate that the signature of an impacted air with higher $PM_{2.5,}$ is characterized by the higher N and S contents relative to the carbon. The black carbon (BC) content of the pig pan area was also significantly higher (11.2 % of the Total C) than the office area (2 % of the total C) and the campus (4-7.8 % of the total C).