Table 1. The $PM_{2.5}$ concentration and its chemical property of the air sample collected in this study. (Units are in $\mu g/m^3$)

Air sample	$PM_{2.5}$	Carbon	Nitrogen	Sulfur	BC	C/N/S
Campus weekdays	17.68-18.91	2.54-4.09	0.84-1.68	1.02-3.01	0.1-0.16	5.9/1.7/1
Campus weekends	26.54-32.44	4.33-5.31	1.87-2.82	2.37-4.19	0.34-0.41	4.3/1.6/1
Expt. Station near pig pan	31.68-43.47	6.37-7.59	4.15-7.61	3.89-6.06	0.71-0.85	3.1/2.8/1
Expt. Station near office	12.48	2.64	0.62	0.19	0.05	36.1/7.3/1

Apart from the bulk chemical information, the MESTA thermograms give the chemical signature pertaining to the $PM_{2.5}$ components. Fig. 1 and 2 show the C, N and S thermograms of the $PM_{2.5}$ samples collected in the city campus and the Quincy Station, respectively. The $PM_{2.5}$ of the campus air is similar chemically between the weekday and weekend samples. Both $PM_{2.5}$ samples have a low-temperature and a high-temperature components. Within the low-temperature component, there was a sulfur containing component and a non-sulfur containing component. The high-temperature component had low nitrogen content and virtually had no sulfur in it. The $PM_{2.5}$ of the Quincy Station near the pig pan area had the similar chemical signature of the campus $PM_{2.5}$, except that the nitrogen content of the low-temperature component was significantly higher in the rural Quincy than in the city campus. The $PM_{2.5}$ chemical signature of the $PM_{2.5}$ in Quincy near the office area was quite different from the rest of the $PM_{2.5}$ samples in that the nitrogen content was found only in the lowest temperature component and the sulfur does not synchronize with C or N. For comparison, we also analyzed the NIST SRM 1649a urban dust standard (Fig. 3). The NIST urban dust standard has also higher nitrogen content organic matter that is in the low-temperature component. In the NIST urban dust standard, there is a nitrogen component that does not synchronize with the carbon and the volatilization temperature is below 200 °C. Detail interpretation of the MESTA thermograms requires further work and analyses. Nonetheless, the MESTA provides new chemical information of the $PM_{2.5}$ samples in a rapid and convenient manner, which is needed in air quality studies.

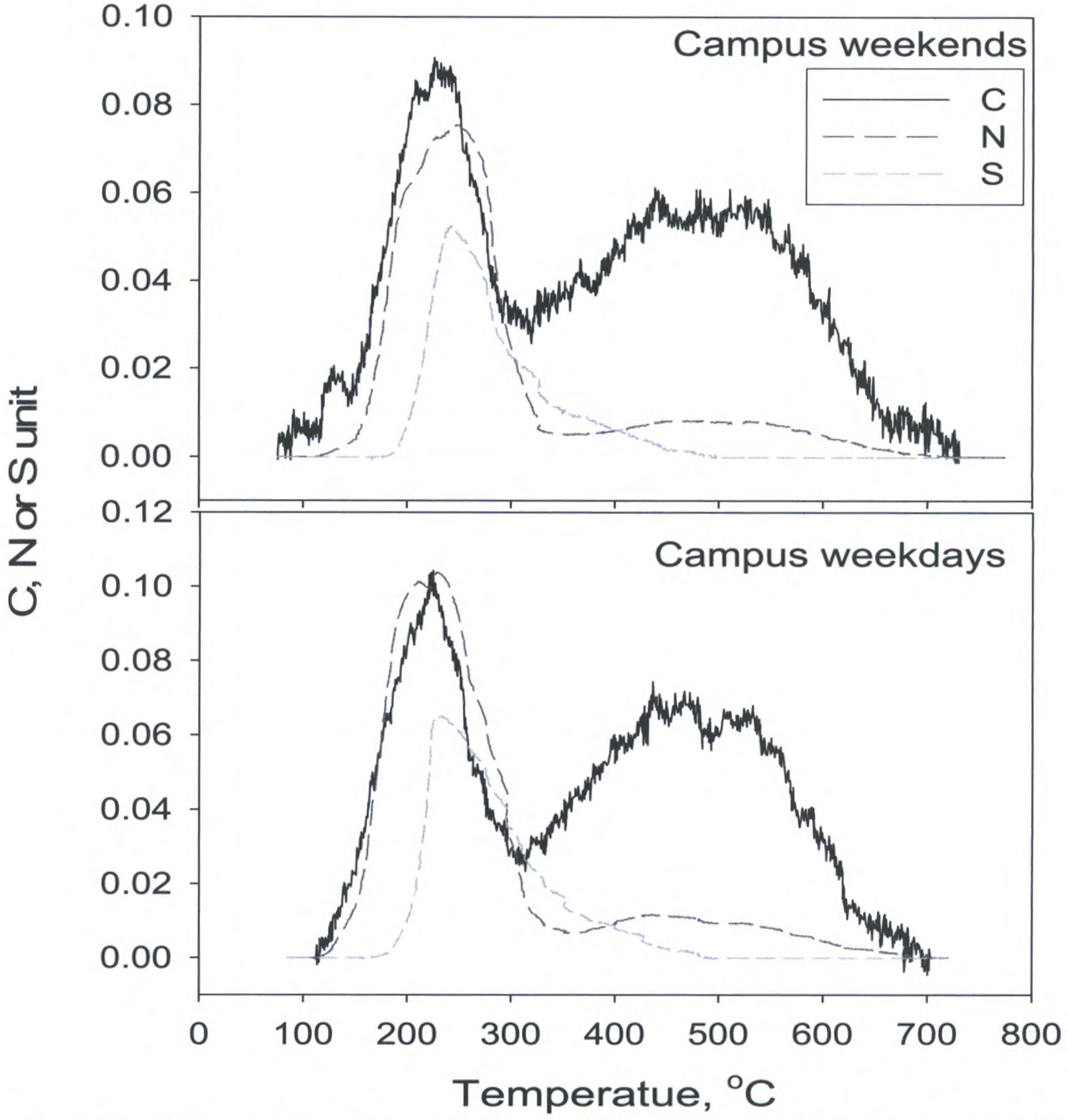

Figure. 1. The C, N and S thermograms of the air $PM_{2.5}$ samples collected during weekdays and weekends, respectively in the Tallahassee Florida A&M University campus. The C, N and S units are expressed proportional to their relative atomic abundance.

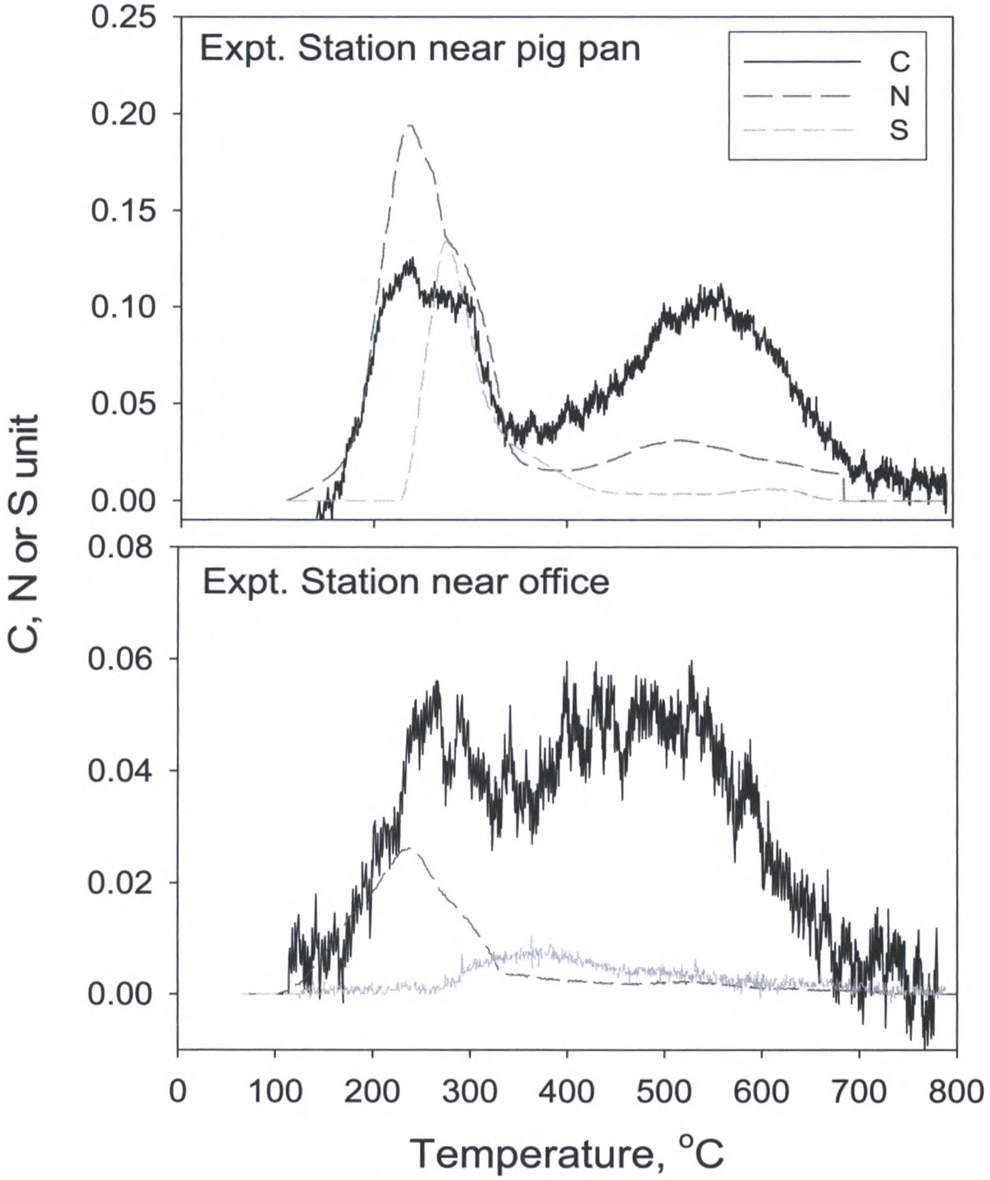

Figure. 2. The C, N and S thermograms of the air $PM_{2.5}$ samples collected from the pig pan area and the office area of the Quincy Experimental Station, respectively. The C, N and S units are expressed proportional to their relative atomic abundance.

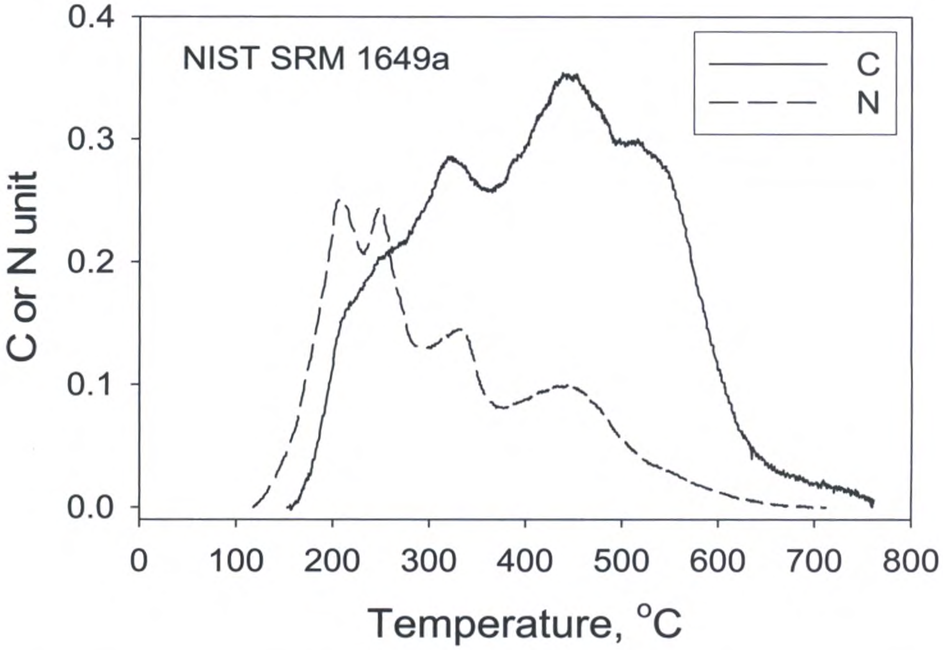

Figure. 3. The MESTA thermograms of the NIST SRM 1649a urban dust standard. The C and N units are expressed proportional to their relative atomic abundance.

Conclusions

Analysis of $PM_{2.5}$ samples collected from the Florida A&M University Tallahassee campus and the Quincy Experimental Station using the MESTA technology reveals that the chemical signatures of the Tallahassee campus and the Quincy Station were quite different in that the relative N and S contents to carbon is much higher in the former than the latter. The $PM_{2.5}$ collected near the pig pan area in the Quincy Station, however, show similarity in chemical signature to that in the city. 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. The results of this study indicate that the newly developed MESTA technology is a rapid and effective way to study $PM_{2.5}$ in the air not only in terms of the bulk chemical property but also in terms of the component chemical properties.

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Ammonia Emissions and their Implications on Fine Particulate Matter Formation in North Carolina

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Abstract

Ammonia (NH_3) is an important atmospheric pollutant that plays a key role in several air pollution problems. The accuracy of NH_3 emissions can have a large effect on air quality model (AQM) predictions of aerosol sulfate, nitrate, and ammonium concentrations. Large uncertainties exist in NH_3 emission inventories in both total emissions and temporal variations. In this work, sensitivity simulations are conducted to assess the impact of NH_3 emissions on the formation of $PM_{2.5}$ and its composition in August and December 2002 in North Carolina.

Introduction

Ammonia in the atmosphere has a large effect on the formation of fine particles, such as aerosol ammonium sulfate and ammonium nitrate, due to its important role in the neutralization of acidic compounds (Seinfeld and Pandis, 1998). Major emission sources of NH_3 include animal waste, human waste, and biogenic soil emissions (Bouwman et al., 1997; Aneja et al., 1998; Goebes et al., 2003). Ammonia emission estimates for the state of North Carolina indicate that livestock and fertilizer together are responsible for about 80-90% of total NH_3 emissions (Wu et al., 2006). Accurate estimates of NH_3 emissions are needed for reliable AQM predictions, but current NH_3 emission inventories are uncertain both in annual estimates and in the monthly, daily, and diurnal variations. Since most ammonia emissions are from non-point sources such as livestock operations and fertilized fields, ammonia emissions from these sources are difficult to measure directly (Gilliland et al., 2003; Pinder et al., 2004 a, b, 2005).

To study the fate of NH_3 and the impact of the agriculture-livestock NH_3 emissions on ambient fine particulate matter ($PM_{2.5}$), two 1-month baseline AQM simulations have been recently conducted using the U.S. EPA Community Multiscale Air Quality (CMAQ) modeling system for August and December, 2002 in a Southeast U.S. domain that covers primarily the state of North Carolina at a 4-km horizontal grid spacing (Wu et al., 2005; 2006). The baseline simulation results are evaluated using the observational datasets from national and state-owned networks such as the Interagency Monitoring of Protected Visual Environments (IMPROVE), the EPA Speciation Trends Networks (STN), the Clean Air Status Trends Network (CASTNet), and the North Carolina Department of Environment and Natural Resources (NCDENR). The evaluation shows underpredictions for $PM_{2.5}$ (with normalized mean bias (NMB) of -31.8% to -45.2%), NH_4^+ (-18.0% to -35.2%), NO_3^- (-40.9% to -64.2%), SO_4^{2-} (-6.2% to -18.7%) in August; and overpredictions for $PM_{2.5}$ (8.8% to 46.7%), NH_4^+ (30.8% to 53.2%), NO_3^- (58.6% to 158.1%), and overprediction for SO_4^{2-} at the IMPROVE sites (9.1%) but underpredictions at the STN (-21.0%) and the CASTNet sites (-4.2%) in December. In addition to the inaccuracies in the simulated meteorological field and the uncertainties in the model treatment for aerosol dynamics and chemistry, the inaccuracies in the estimation of NH_3 emissions can have a large effect on the model performance on ammonium, nitrate, and $PM_{2.5}$. A comprehensive evaluation of both meteorological and chemical conditions along with a detailed process analysis for the baseline simulations in August and December 2002 are being performed (Krishnan et al., 2006; Wu et al., 2006). The relative importance of meteorological and chemical processes is being examined. The likely reasons for the discrepancies between the simulated and observed meteorological variables and chemical concentrations are being identified.

Summary of Sensitivity Simulations and Results

Differences exist in the domainwide total NH_3 emissions provided by different emission inventories due likely to different approaches used to create the emission inventories and different source categories, strengths, and emission factors included. For example, in the baseline simulations, the domainwide total NH_3 emissions are based on the emission inventory developed by the Visibility Improvement State and Tribal Association of the Southeast (VISTAS) (Morris and Koo, 2004). It gives a domainwide total of 568 tons per day in August and 334 tons per day in December. The Carnegie Mellon University (CMU) inventory (Goebes et al., 2003; Pinder et al., 2004b; Strader et al., 2005), on the other hand, gives a domainwide total of 735 tons per day in August and 226 tons per day in December. Using the CMU inventory as a benchmark, two methods have been applied to adjust the baseline NH_3 emissions that are based on the VISTAS emission inventory (referred to as Baseline hereafter). The first method is to use the total CMU NH_3 emissions but still keep the same diurnal varibility as the baseline simulations (referred to as Sen_uniform hereafter), namely, multiplying the baseline VISTAS total NH_3 emissions by a domainwide uniform factor of 1.29 for August and by 0.68 for December to match the total CMU NH_3 emissions. The second method is to use the total CMU NH_3 emissions and the CMU diurnal varibility (referred to as Sen_diurnal hereafter), namely, replacing the hourly NH_3 emission rates in the baseline simulations by those of the CMU inventory. The difference between Sen_uniform and Sen_diurnal lies in the diurnal variability profiles used, namely, Sen_diurnal gives higher daytime emission rates and lower nighttime emission rates than those of Sen_uniform in August, and has emission rates that are higher between 1-10 a.m., lower between 4 p.m.-11 p.m., and similar between 10 a.m.-4 p.m. in December. Sensitivity simulations with the two emission adjustment methods are performed to study the sensitivity of the concentrations of $PM_{2.5}$ and ammonium salts to the NH_3 emission adjustments in August and December, 2002. The sensitivity simulation results are evaluated in terms of spatial distributions, temporal variations, and the overall statistical performance.

The results of the sensitivity simulations show a large spatial and temporal variation of the impact of NH_3 emissions on PM ammonium and nitrate formation. In addition to emissions, other influential factors such as meteorological conditions and ambient chemical conditions are being analyzed along with the impacts of NH_3 emission adjustments. The statistical results show that the two emission adjustment methods improve the overall model performance in both August and December. For example, the NMBs of NH_4^+ change from -18.0% (Baseline) to -10.7% (Sen_uniform) and -11.8% (Sen_diurnal) in August and from 30.8% (Baseline) to 15.6% (Sen_uniform) and 16.8% (Sen_diurnal) in December at STN sites and from -35.2% (Baseline) to -28.6% (Sen_uniform) and -28.7% (Sen_diurnal) in August and from 53.2% (Baseline) to 41.9% (Sen_uniform) and 42.1% (Sen_diurnal) in December at IMPROVE sites. The correlation coefficients from the two sensitivity simulations remain the same as or similar to those from the baseline simulations for all species except NH_4^+, whose correlation coefficient is slightly improved, changing from 0.81 to 0.86 and 0.85 for Sen_uniform and Sen_diurnal in August.

To identify the possible reasons for the similar performance of the two emission adjustment methods, we further analyze the predicted hourly $PM_{2.5}$ concentrations with the hourly observations that are available only at one NCDENR site, i.e., Grainger (GR) 371190041 site, in August. The statistics calculated for the GR 371190041 site show that Sen_uniform and Sen_diurnal give mean hourly $PM_{2.5}$ concentrations of 13.76 and 13.79 $\mu g\ m^{-3}$, respectively, and NMBs of -19.4% and -19.2%, respectively, during the daytime. During the nighttime, i.e., Sen_uniform and Sen_diurnal give mean hourly values of 13.88 and 13.79 $\mu g\ m^{-3}$, respectively, and NMBs of -19.6% and -20.1%, respectively. For comparison, the baseline simulation gives a mean hourly $PM_{2.5}$ concentration of 13.52 $\mu g/m^3$, with a NMB of -20.8% during the daytime and a mean hourly $PM_{2.5}$ concentration of 13.73 $\mu g/m^3$, with a NMB of -20.5% during the nighttime. The correlation coefficients for the two sensitivity simulations are the same as those of the baseline simulations. Two sensitivity simulations show similar predictions on hourly $PM_{2.5}$ concentrations to those of the baseline simulation, partially due to the fact that ammonium and nitrate account for only about 10% of the total $PM_{2.5}$ mass at this site, and the changes in the concentrations of ammonium and nitrate as a result of the emission adjustments in the two sensitivity simulations may be too small to change the predicted $PM_{2.5}$ concentrations appreciably. Another possible reason is that the site is located in ammonia-rich regime where there are sufficient amounts of ammonia to neutralize sulfate and nitrate ions. In such a regime, the increased amount of NH_3 will not result in a significant conversion to particulate NH_4^+. The differences in the predicted concentrations of ammonium and nitrate between the two sensitivity simulations, therefore, are overall not statistically significant at this site, resulting in similar $PM_{2.5}$ concentrations by the two simulations. More detailed analyses are being conducted to fully understand all major reasons for the similar performance of the two emission adjustment methods.

Acknowledgements

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Aerial Pollutants Emissions from Confined Animal Buildings

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Abstract

A multi-state project entitled "Air Pollutants Emissions from Confined Animal Buildings" (APECAB) measured baseline emission rates of odor, ammonia (NH_3), hydrogen sulfide (H_2S), carbon dioxide (CO_2) and particulate matter (including total suspended particulate (TSP) and PM_{10}) from six types of animal confinement buildings (2 barns from each type) located in different states. The following types of animal housing systems were studied: swine farrowing with pull-plug gutters (IL), sow gestation with pull-plug gutters (MN), swine finishing with deep pits (IA), swine finishing with pull-plug gutters (TX), conventional high-rise laying hen houses (IN), and broiler houses on floor litter (NC). Air sampling from two adjacent identical buildings for each type was conducted from winter 2003 through spring 2004. Measurements were semi-continuous for NH_3, H_2S, and CO_2, continuous for PM_{10}, and discrete for odor and TSP. Quality assurance and control (QAQC) procedures for data collection and analysis and protocol consistency between states were emphasized. Ammonia levels in the finishing barns were twice as high in the deep pit barns (20 ppm) compared to the pull plug (9 ppm) facility but H_2S concentrations were similar in both types of barns, varying from 0.4 to 0.6 ppm. NH_3 emissions from the deep pit finishing barns were also higher (50 to 60 g NH_3/d-AU) than from the pull plug building (35 to 40 g NH_3/d-AU) but H_2S emissions were somewhat similar, 3.0 to 4.0 and 4.0 to 4.5 g H_2S/d-AU for the pull-plug and deep-pit barns respectively. The pull plug finishing barns experienced higher PM_{10} concentrations (450 to 500 vs. 150 to 170 μg PM_{10}/m^3) and emissions (3.0 vs. 0.75 g PM_{10}/d-AU) than the deep pit finishing barns. However, the deep-pit barns had higher odor concentrations (1350 to 1650 vs. 600 to 750 OU/m^3) and emissions (87 to 93 vs. 66 to 80 OU/s-AU) than the pull-plug finishing buildings. Although not specifically reported in this paper, the laying hen buildings monitored in the project had much higher ammonia concentrations and emissions (by an order of magnitude) than the pig barns monitored but had very low hydrogen sulfide concentrations and emissions when compared to pig facilities. Also, some short term spikes in gas/PM/odor concentrations and emissions were found that typically were caused by some weather or manure management event and which could have ramifications when dealing with meeting the EPA's CERCLA and EPCRA reporting requirements. As a general rule, the magnitude of the gas and dust emissions measured in this study, did not vary much over the year, however the concentrations of these parameters were quite seasonal with high levels in the winter during times of low air exchange rates and low levels in the summer when high rates of ventilation air was provided.

Introduction

U.S. livestock and poultry producers are increasingly concerned over gases and particulates that are generated and emitted from their animal operations. Of primary interest is the reporting requirement of the Environmental Protection Agency's (EPA) Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and the Emergency Planning and Community Right-to-Know Act (EPCRA) if an animal production facility exceeds the 45 kg/d threshold of a hazardous material. Ammonia and hydrogen sulfide are generally considered the hazardous gas compounds of concern for animal operations. In addition, the Clean Air Act may restrict other volatile organic compounds (VOCs) and particulate material or dust with a mass medium diameter of 10 microns or less (PM_{10}) emitted from the animal production system to 90 metric tons/yr. Although these regulations have been in place for some time, state and federal regulatory agencies have not enforced them for livestock and poultry operations. The lack of enforcement is due to the limited research information on the amount of airborne contaminants being emitted from animal facilities and associated manure storage units.

Unfortunately, quantifying air emissions from animal facilities is difficult. First, the complexity arises from the multitude and variety of individual sources responsible for emissions, the extreme variability of these emissions, and the variety of gaseous components being emitted. Secondly, the methods used to collect emission data, from sources like animal buildings, have not been standardized and involve the measurement of both the concentrations of the contaminant and the airflow rate. For these reasons, relatively few studies have reported on ammonia (NH_3), hydrogen sulfide (H_2S), dust (PM_{10}), and odor emission rates from U.S. animal facilities. Casey et al. (2005) reviewed the values reported in the literature for these three air pollutants as well as several others. They concluded that wide variations exist in all types of air emissions because of seasonal, diurnal, species, and other factors.

A heightened concern has been expressed about the estimated ammonia emissions from U.S. agricultural sources derived from the European literature (Battye et al. 1994) Only a few U.S. researchers (Gay et al. 2002, Ni et al. 2000, and Stowell, et al. 2000) have measured ammonia emissions in the United States and have generally found lower values than reported by Battye (Sweeten et al. 2000). Certainly, there is a need for more information on ammonia and other air emissions from US animal facilities.

To address the need for gas, odor, and PM emission from actual animal production buildings, funding was secured by a six-state research team for a USDA project entitled "Air Pollutants Emissions from Confined Animal Buildings," or APECAB. The main objective of APECAB was to quantify long-term (yearly) air pollutant emissions from confined animal buildings and establish methodologies for real time measurement of these emissions and build a valid database of air emissions for US livestock and poultry buildings.

Experimental Methods

The APECAB study is a collaboration of land-grant universities in Minnesota, Indiana, Illinois, Texas, Iowa, and North Carolina. The project was initially funded by the USDA-CSREES in the fall of 2001. Extensive planning occurred in the next nine months for protocol development and equipment selection and purchase. Data collection began at various times in the fall of 2002 for each of the cooperating universities. Data collection concluded in the spring of 2004 and the project ended in the fall of 2005. The goal of the study was a 15-month sampling period to assure that long-term emissions values from actual animal production buildings were determined. Long-term measurements result in recording the variations in emissions due to seasonal effects, animal growth cycles, diurnal variations, and in-house manure storage levels.

The study utilized common instrumentation and protocol. At each measurement site, an instrument trailer was stationed between two similar, mechanically-ventilated, confined animal production buildings and emission measurements were quasi-continuous for gas and continuous for particulate matter (Jacobson et al. 2004) Four swine (finishing, gestation, and farrowing production stages) sites were selected along with two poultry (layer and broiler) sites.

The instrument trailer housed: a gas sampling system (GSS), gas analyzers, environmental instrumentation, a computer, data acquisition system, controller units for PM_{10} monitors, calibration gas cylinders, and other supplies. The specific gas and PM instrumentation included the following:

NH_3 - a chemiluminescence NO_x analyzer with NH_3 converter, Model 17C, Thermal Environmental Instruments (TEI), Franklin, MA

H_2S - a pulsed fluorescence SO_2 detector with H_2S converter, Model 45C, Thermal Environmental Instruments (TEI), Franklin, MA

CO_2 – two photo acoustic infrared CO_2 analyzers (2,000-ppm & 10,000-ppm), Model 3600, Mine Safety Appliances (MSA), Co., Pittsburg, PA

PM_{10} – two "tapered element oscillating microbalances" or TEOM ambient PM_{10} monitors, Model 1400a, Rupprecht & Patashnick, Albany, NY

Gas concentrations (Heber et al. 2002a) were measured at the air inlets and outlets of each building through the use of the GSS. PM_{10} was measured continuously by the TEOM (Heber et al.2002b). Odor samples were taken biweekly and analyzed within 24 hours at olfactometry laboratories to determine odor concentrations and to calculate resulting emissions (Jacobson et al.2002)

Ventilation rates were measured at each site using procedures described in Hoff et al. (2004). The measurement of ventilation rate is critical in calculating an emission rate. In general, the ventilation rates are calculated by using the fan status (on, off, or RPM), the barn static pressure, and the measured fan curves. Each site had a Fan Assessment Numeration System (FANS) system that was used to measure the actual performance of the fans as found at each barn.

Emission rates were calculated by multiplying concentration differences between inlet and outlet air by standardized building airflow rates (dry standard m^3/s). The standard conditions, STP, used in this study were a temperature of 20°C, dry air, and a barometric pressure of 101,325 Pa. As an example, the gas emission rate was calculated as:

$$E = Q_o'*C_o' - Q_i'*C_i' \qquad \text{Equation 1}$$

where:

E = Barn emission rate, mg/s or μg/s

Q_o' = Dry standard ventilation rate at barn exhaust (based on STP), dsm^3/s

C_o' = Standardized mass concentration at the barn exhaust (based on STP), mg/dsm^3 or $\mu g/dsm^3$

Q_i' = Dry standard ventilation rate at the barn inlet (based on STP), dsm^3/s

C_i' = Standardized mass concentration at the barn air inlet (based on STP), mg/dsm^3 or $\mu g/dsm^3$

In this study, each gas analyzer was automatically and sequentially switched to sample air from up to 12 sampling location groups (SLG). Gas concentrations of each SLG were measured continuously during a 10-min sampling period before switching to the next SLG. For sampling cycles with 12 SLGs, gas concentrations were therefore measured during twelve, 120-min sampling cycles per day. The pre-equilibration gas concentration readings during each sampling period are flagged invalid while the gas concentration readings during the remainder of the sampling period are valid (Heber, et al. 2001) The number of invalid readings depends on the time required for equilibrium, which varies depending on the analyzer and its condition. The following invalid and valid periods for each analyzer were generally used at the six sites for each 10-min sampling period:

Ammonia	7 min invalid, 3 min valid
Hydrogen Sulfide	5 min invalid, 5 min valid
Carbon Dioxide	3 min invalid, 7 min valid

The analyzers were calibrated at least weekly with EPA certified calibration gas cylinders. As the calibration would change during the week, the recorded gas concentrations were adjusted to reflect a linearly interpolated calibration from week to week. The valid gas concentrations from each SLG were averaged and then linearly interpolated between each concentration measurement (generally 120 min). The interpolated concentration data was then combined with the continuous airflow data in order to create a continuous emission data set. Furthermore, to avoid bias due to partial data days (data was unusable due to calibration or other reasons), a policy requiring at least 70% valid data for calculating average daily averages for a complete-data day was established. Similarly, hourly averages were only reported if at least 70% of the data during that hour were valid and monthly averages were reported only if at least 70% of the days were valid.

Results and Discussion

The data reported in this discussion represents the work from four of the six sites in the APECAB project. The four sites consisted of:

Two 650-head pull-plug sow gestation barns in Minnesota

Two 60-crate pull-plug farrowing rooms in Illinois

Two 1080-head pull-plug finishing barns in Texas

Two 960-head deep-pit finishing barns in Iowa

The average NH_3 concentration and emission results for the above facilities are shown in figures 1 and 2. This data represents approximately one year of measurements at the four different sites. The following figures represent only the buildings; with the exception of the deep-pit (DP) finishing barns, which includes underfloor manure storages that generate additional emissions. The gestation, farrowing, and one of the finishing sites utilized pull-plug (PP) manure handling systems. As shown in figures 1 and 2, the farrowing rooms had the lowest NH_3 concentrations and emission per AU (animal unit = 500 kg of animal weight). This would be expected as indoor air quality is emphasized in farrowing rooms.

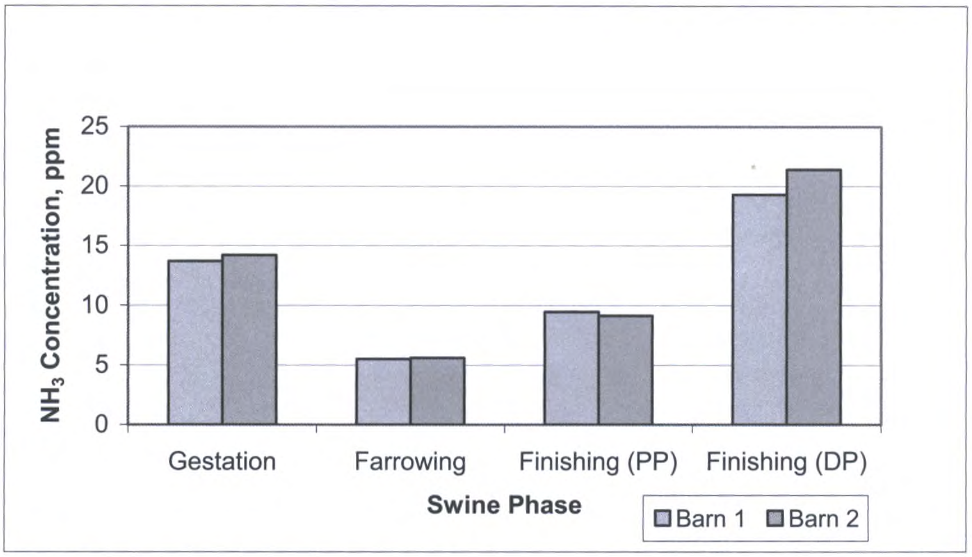

Figure 1. Average Ammonia Concentrations

The average NH_3 concentration measured in the farrowing rooms was 5.6±2.4 ppm and the average ammonia emission was 12±6 g/d-AU (average±st.dev). In the Minnesota gestation barns, the average NH_3 concentration was 13.9±7.7 ppm with an emission rate of 19±7 g/d-AU. NH_3 concentrations in the two finishing sites were quite different as the Texas PP site had an average ammonia level of 9.3±4.3 ppm and the Iowa DP site was at 20.4±12.0 ppm of NH_3. This concentration difference in ammonia could partially be explained by the different manure handling systems and due to the differences in ambient temperatures that are used to control ventilation rates. The average ambient Texas temperature was 13.6±9.4°C whereas the Iowa site's mean temperature was 7.0±11.9°C during the monitoring period. The average NH_3 emission at the Texas site was 39±16 g/d-AU and at the Iowa site, the NH_3 emission was 56±24 g/d-AU. The lower building emission for NH_3 for the Texas PP site compared to the Iowa DP site may also be partially explained by the existence of lagoon manure storage at the Texas site.

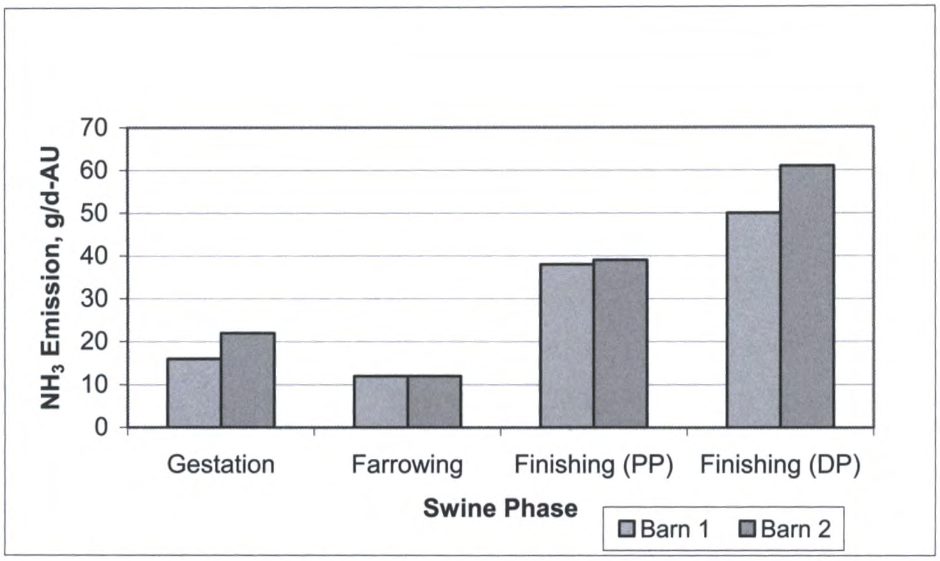

Figure 2. Average Ammonia Emissions

The hydrogen sulfide concentration results again were lowest for the Illinois farrowing rooms with an average H_2S concentration of only 292±148 ppb as shown in figure 3. The H_2S concentrations found in the gestation and the two finishing facilities were quite similar and are approximately double that of the farrowing rooms. The gestation barns had an average H_2S concentration of 591±185 ppb. The PP finishing site had a H_2S concentration of 588±611 ppb and the DP finishing site had a H_2S concentration of 434±234 ppb. Figure 4 represents the H_2S emissions and indicates that the gestation and farrowing facilities were similar to each other on a per AU basis. The gestation barns had an average H_2S emission of 1.5±0.8 g/d-AU and the farrowing rooms also had an emission of 1.5±0.7 g/d-AU. The two finishing facilities had a H_2S emission rate of 4.3±2.8 and 3.4±3.0 g/d-AU for the PP and DP sites, respectively.

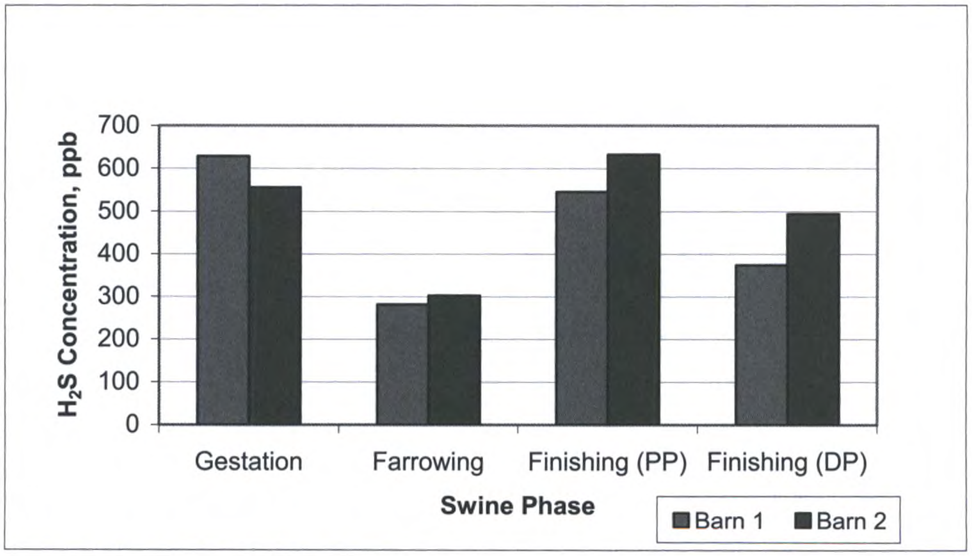

Figure 3. Average Hydrogen Sulfide Concentrations

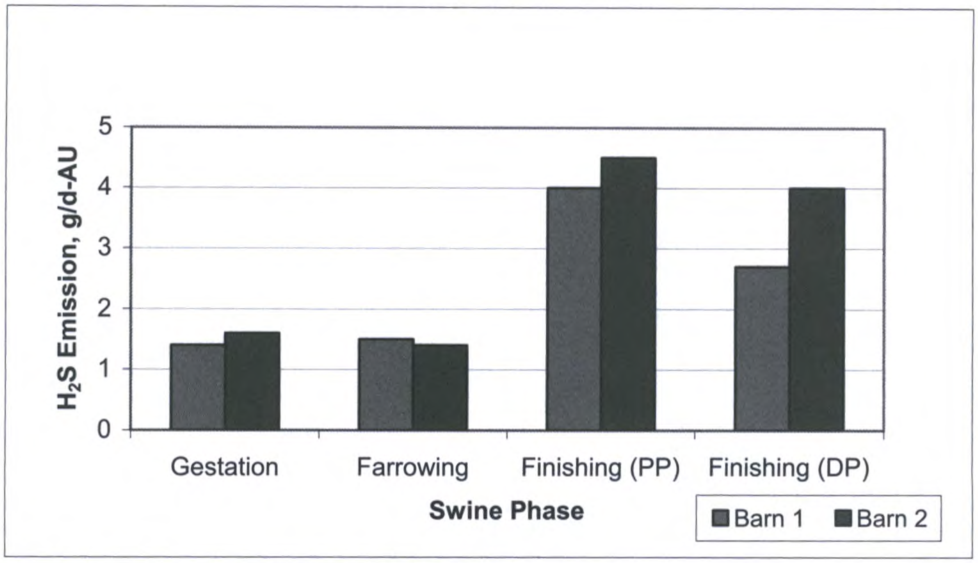

Figure 4. Average Hydrogen Sulfide Emissions

The results of the PM_{10} measurements for these four sites are shown in figures 5 and 6. The Iowa DP finishing barns were the lowest in both PM_{10} concentrations and emissions with averages of 158±102 □g/m^3 and 0.8±0.6 g/d-AU respectively. The Texas PP finishing barns had a higher average PM_{10} concentration (467±238 □g/m^3) and greater PM_{10} emissions (3.0±1.0 g/d-AU) than the Iowa barns. The differences between the two finishing facilities could be a result of a combination of relative humidity differences, animal diet (i.e. presence of fat), or numerous other factors.

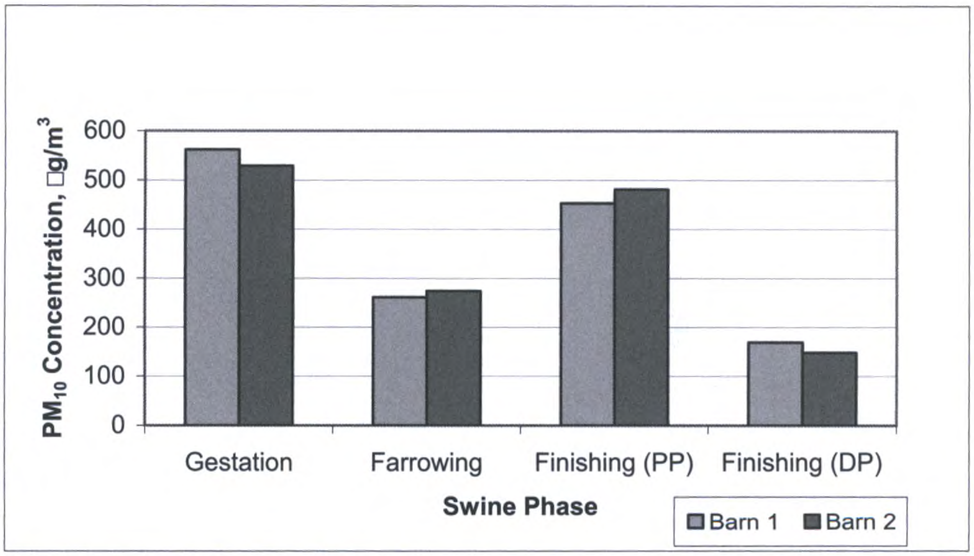

Figure 5. Average PM_{10} Concentrations

The gestation barns had the highest average PM_{10} concentration of 545±240 □g/m^3 as compared to the other three swine facilities but similar emission levels to the farrowing and DP finishing. The gestation barns had individual sow crates and feeders, which could contribute to the higher PM_{10} concentrations during filling and sow feeding events. The farrowing rooms had an average PM_{10} concentration of 267±179 mg/m^3 with an average emission of 1.2±1.1 g/d-AU.

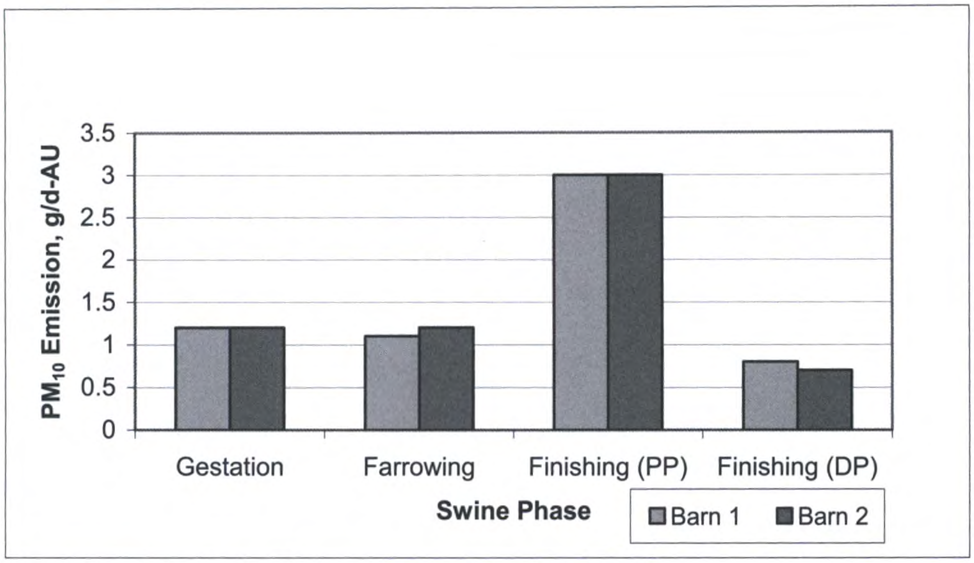

Figure 6. Average PM$_{10}$ Emissions

The Iowa DP finishing barns had both the highest odor concentration and emission in comparison to the other swine sites. Certainly storing manure beneath the barn's 100% concrete slatted floor probably contributed to higher odor generation. The Iowa DP site had an average odor concentration of 1490±640 OU/m^3 with an associated emission rate of 90±83 OU/s-AU. The Texas PP finishing site had a lower average odor concentration of 680±200 OU/m^3, however the emission rate for odor (73±79 OU/s-AU) was only slightly lower than the Iowa site. The Illinois farrowing rooms had the lowest odor concentration and emission rates with averages of 620±570 OU/m^3 and 43±29 OU/s-AU, respectively. The gestation barns had an average concentration of 970±630 OU/m^3 and an emission rate of 45±38 OU/s-AU. The higher odor emissions found in the finishing barns are possibly due to greater animal activity and growth rates and subsequently greater manure generation by the animals.

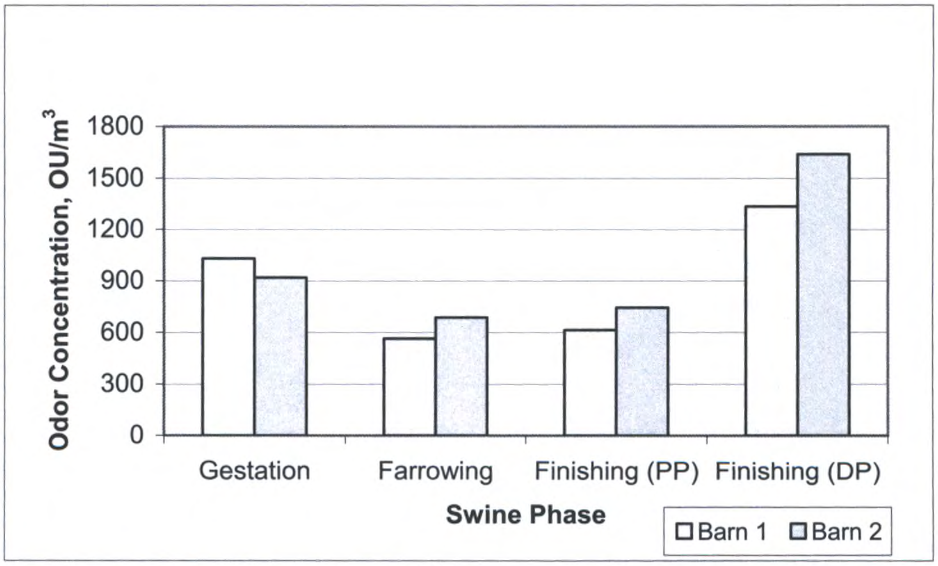

Figure 7. Average Odor Concentrations

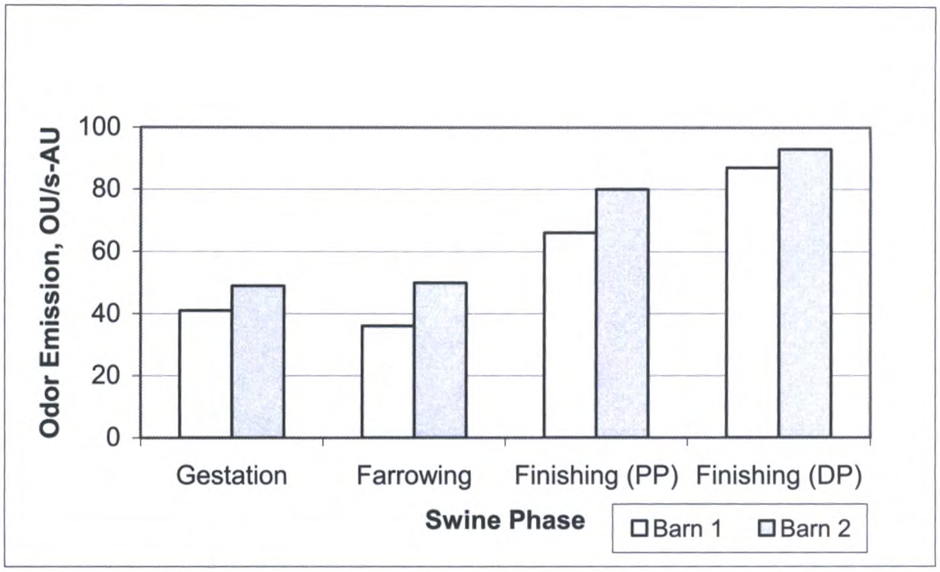

Figure 8. Average Odor Emissions

The maximum daily averages of the gases and particulate matter are shown in tables 1 and 2. The data in table 1 could be useful in determining if a given site exceeds the reporting threshold for NH_3 and H_2S of 45 kg/d under CERCLA and EPCRA, since theoretically only a single day's emissions would be required. In general, NH_3 will be the gas that will trigger the reporting requirements. Per AU, the finishing sites had much higher daily maximums than the gestation and farrowing sites. The maximums for the DP finishing site were higher than the PP finishing site for NH_3, H_2S, and odor. The PM_{10} and odor maximums listed in table 2 are shown as upper limits for particulates and odor that were found in this study.

Table 1. Maximum daily concentration and emission averages for NH_3 and H_2S.

Daily Max	**NH_3, ppm**		**NH_3, g/d-AU**		**H_2S, ppm**		**H_2S, g/d-AU**	
	Barn 1	Barn 2	Barn 1	Barn 2	Barn 1	Barn 2	Barn 1	Barn 2
Gestation	33.5	31.5	48	48	15.0	13.9	7.8	5.4
Farrowing	11.7	12.5	27	34	0.79	0.82	4.2	3.5
Finishing (PP)	22.3	20.7	77	81	26.2	31.5	13.2	15.0
Finishing (DP)	47.9	57.5	102	130	19.7	15.6	30.8	19.4

Table 2. Maximum daily concentration and emission averages for PM_{10} and Odor.

Daily Max	**PM_{10}, □g/m3**		**PM_{10}, g/d-AU**		**Odor, OU/m^3**		**Odor, OU/s-AU**	
	Barn 1	Barn 2	Barn 1	Barn 2	Barn 1	Barn 2	Barn 1	Barn 2
Gestation	1030	1070	3.7	2.5	2580	2510	140	140
Farrowing	710	660	4.4	8.6	1870	2220	93	120
Finishing (PP)	1220	1500	5.7	5.7	2090	2020	350	300
Finishing (DP)	500	410	4.0	2.9	2940	4250	370	320

Conclusions

Ammonia levels in the finishing barns were twice as high in the deep pit barns (20 ppm) compared to the pull plug (9 ppm) facility but H_2S concentrations were similar in both types of barns, varying from 0.4 to 0.6 ppm. NH_3 emissions from the deep pit finishing barns were also higher (50 to 60 g NH_3/d-AU) than from the pull plug building (35 to 40 g NH_3/d-AU) but H_2S emissions were somewhat similar, 3.0 to 4.0 and 4.0 to 4.5 g H_2S/d-AU for the pull-plug and deep-pit barns respectively. The pull plug finishing barns experienced higher PM_{10} concentrations (450 to 500 vs. 150 to 170 □g PM_{10}/m^3) and emissions (3.0 vs 0.75 g PM_{10}/d-AU) than the deep pit finishing barns. However, the deep-pit barns had higher odor concentrations (1350 to 1650 vs. 600 to 750 OU/m^3) and emissions (87 to 93 vs. 66 to 80 OU/s-AU) than the pull-plug finishing buildings. Although not specifically reported in this paper, the laying hen buildings monitored in the project had much higher ammonia concentrations and emissions (by an order of magnitude) than the pig barns monitored but had very low hydrogen sulfide concentrations and emissions when compared to pig facilities. Also, some short term spikes in gas/PM/odor concentrations and emissions were found that typically were caused by some weather or manure management event and which could have ramifications when dealing with complying with the EPA's CERCLA and EPCRA reporting requirements. As a general rule, the magnitude of the gas and dust emissions measured in this study, did not vary much over the year, however the concentrations of these parameters were quite seasonal with high levels in the winter during times of low air exchange rates and low levels in the summer when high rates of ventilation air was provided.

Acknowledgements

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Bactericidal and Antiviral Effectiveness of the Product 3B™ in the Treatment of Served Waters, Cattle Feces, and Drinkable Water

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Abstract

It was performed the evaluation of the effectiveness of the 3B® product in the inhibition of bacterial and antiviral growth. The 3B® is an equilibrated mixture of controlled strong and weak acids, of pH <1 and innocuous to the human tissues and mucous. The study determined in vitro its inhibitory effectiveness on the growth of microorganisms in water of Maracaibo Lake, served waters taken from the outlet of the clarifier of water treatment plant located in Maracaibo, Venezuela, The same evaluation using 3B in cattle fecal feces in three concentrations High (Non diluted) Medium (diluted 1:50 ml of Water) and Low (diluted in 1:100 ml of water). The results of the in vitro tests with all cultured water and after 24 hours of contact express the total inhibition (0nmp/100 ml) of microorganisms. The results of the culture with cattle fecal feces and after 72 hours of direct contact resulted on the total inhibition of the microorganisms *Proteus sp.*, *Escherichia coli*, *Klebsiella pneumoniae*, *Bacillus* Gram negative, *Enterobacter aerogenes*, *Enterobacter cloacae*, Filamentous Fungus and the absolute and fast disappearance of feces odor.

The Use of Sodium Bisulfate as a Best Management Practice for Reducing Ammonia and VOC Emissions from Poultry and Dairy Manures

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Abstract

Sodium bisulfate is used extensively by commercial broiler integrators and growers in the United States, Canada, and Latin America to reduce ammonia and pathogen levels in the presence of birds as a Best Management Practice for animal welfare and bird health. This paper will discuss the usage of sodium bisulfate as a Best Management Practice for reducing ammonia emissions from both commercial broiler and commercial layer facilities and the economic benefits in bird production associated with its use. Data from an ongoing 2-yr ammonia emissions study in a broiler facility in Georgia will be presented along with data on ammonia emissions and fly control from a commercial egg facility in Pennsylvania. The use of sodium bisulfate for reducing ammonia and VOC emissions from dairy manure will also be discussed.

Introduction

The production of ammonia (NH_3), volatile organic compounds (VOCs) and greenhouse gases (GHG) by animal manures has received increased scrutiny by both state and national regulatory agencies and the community-at-large. These gaseous releases are produced by microbial activity on the nitrogen and carbon compounds not utilized by the animals for either maintenance or growth and excreted in the feces and /or urine (Carey, et al., 2004; Mutlu, et al. 2005). While much debate continues in the United States at the Federal level regarding both the applicability of CERCLA/EPCRA reporting limits for gases derived from animal manures and whether or not NH_3 should be defined as a precursor pollutant to PM 2.5 under the Clean Air Act (CAA), State governments and the courts, most noticeably in California, have decided to regulate gaseous emissions from animal agriculture under both environmental pollution and nuisance odor statutes.

This has left livestock and poultry producers with the need to implement effective best management practices to control both ammonia and VOCs emissions from animal housing and manure storage facilities (Dragosits, et al. 2002). This is also critical to European livestock & poultry producers as the BMPs implemented there were not enough to reach the emissions targets set in the Netherlands for the year 2000. It has been suggested that the only way to reach the target goals for NH_3 emissions ($30GgNH_3/yr$) set for 2030 in the Netherlands would be to completely eliminate all poultry & swine production and house all cattle in low-emission stables year-round (de Vries, et al. 2001). In addition, tremendous consumer focus on animal welfare has instituted strict limits on ammonia levels inside confinement animal facilities, mostly poultry & swine. Since the current management strategies often rely on being able to exhaust as much ammonia from the house as possible, alternatives are clearly needed (Ritz, et al. 2004).

The release of ammonia from animal manure is dependent upon the amount of ammoniacal nitrogen present, pH, surface area, temperature, and the amount of urease present (Mutlu, et al., 2005; Gay and Knowlton, 2005). Therefore, for any emissions intervention to be effective, it must exploit at least one of these avenues to prevent NH_3 release into the atmosphere (Jongebreur and Monteny, 2001). VOCs are mostly derived from the bacterial degradation of manures soon after excretion (Mitloehner, 2005). Decreasing the bacterial activity in freshly excreted manures should then reduce the production & subsequent emissions of VOCs.

Sodium Bisulfate Characteristics

Sodium bisulfate (SBS) is a dry, granular acid salt that has been used for many years as a pH reducer in a variety of agricultural, industrial, and food applications. The anti-bacterial properties of sodium bisulfate have been exploited in its application as a toilet-bowl sanitizer (i.e. EPA Reg #1913-24-AA) and as a preservative in EPA method #5035 "Closed-System Purge-and-Trap & Extraction for Volatile Organics in Soil & Waste Samples," to prevent microbial activity leading to VOC release. These properties along with the safety and ease of use of SBS have led to its use for ammonia binding (Fig.1) and bacterial reduction in poultry, dairy, and equine manure and bedding materials (Ullman, et al., 2004; Blake and Hess, 2001; Sweeney, et al., 1996; Harper, 2002). Currently, 30-40% of all broilers produced in the United States are raised on SBS (PLT® litter acidifier, Jones-Hamilton Co., Walbridge, OH) for the purpose of controlling interior ammonia levels and reducing bacterial levels in the litter for bird welfare and performance reasons. Additional research is ongoing to modify the current SBS-BMP used for production purposes to a BMP that maximizes ammonia emissions reductions in poultry & dairy, VOC emissions reductions in dairy, and fly control in egg-layers using SBS. Sodium bisulfate has been widely tested to establish efficacy as both an ammonia controlling agent and a bacterial reducer.

100 lbs. Of SBS Binds 14 lbs. NH_3						
2 $NaHSO_4$	+	$2NH_4OH$	→	$(NH_4)_2SO_4$	+ Na_2SO_4	+ $2H_2O$
100 lbs.		29 lbs.		55 lbs.	59 lbs.	15 lbs.

Figure 1. Binding of Ammonia by SBS to produce Ammonium Sulfate

Ammonia emission from animal housing is calculated by multiplying ammonia concentration by airflow. The use of sodium bisulfate reduces ammonia emissions two ways: by reducing ammonia flux from the surface of the poultry litter and by reducing ventilation rates. Sodium bisulfate is hygroscopic. As water is adsorbed into the SBS bead from the humidity in the air, the SBS is dissolved into its Na^+, H^+, and $SO_4^=$ constituents. The hydrogen ion reduces the pH of the litter and protonates the ammonia molecule. The resulting ammonium is then bound by the sulfate component. This formation of ammonium sulfate is non reversible therefore the nitrogen in the litter is not released as the pH increases (Ullman, et al., 2004). The sodium and hydrogen ions exert negative pressure on the bacterial populations of the litter; decreasing total aerobic population counts 2-3 logs (Pope and Cherry, 2000). This may also serve to decrease urease concentration in the litter for additional ammonia reductions (Ullman, et al., 2004). Once the ammonia concentration at bird level has been reduced, the poultry houses can be minimally ventilated for relative humidity control as they were designed rather than over-ventilated for NH_3 removal (Czarick and Lacey, 1998).

SBS Use in Poultry- Literature Review

Reduction of ambient ammonia levels in broiler housing has been demonstrated in a variety of studies. Pope and Cherry (2000) applied PLT® litter treatment 12-24 hours prior to bird placement at a rate of 2.27 kg/9.29m^2 in three houses each on two 12-house farms. The average litter pH was 1.2 in the houses treated with PLT compared with 8.0 in the untreated controls. Ammonia levels were 90% lower post PLT application with an average of 6.2 PPM of NH_3 in the treated houses and 62.3 PPM in the control houses. Two weeks after application, the ammonia levels in the treated houses were still reduced by 50% compared to control houses. In the winter of 1996, 200 commercial broiler houses were studied in Delaware and Maryland by Terzich (1997) with 100 houses treated with PLT® and 100 houses serving as control. Ammonia levels averaged 127 PPM pre-treatment and were all 0 PPM post-treatment (Table 1). Consequent to the improved air quality, bird performance was significantly improved in the treated houses (1,282,256 birds) with better mortality rates, average weights, average daily gain, and percentage of respiratory lesions at processing compared to controls (1,219,918 birds). Fuel usage was also reported to be 43% less in the treated houses. At a cost of $120/house for the PLT® litter treatment, the resulting production increases and fuel savings provided the producer with a substantial return on investment that would support increased PLT addition rates to maximize ammonia emissions reductions while maintaining producer profitability. Similar ammonia results and improvements in respiratory health through the use of PLT have also been reported (Terzich et al, 1998; Terzich et al, Apr 1998).

Table 1. Average ammonia levels and litter pH values in 100 houses in which litter was treated with sodium bisulfate compared with 100 houses that were untreated controls.

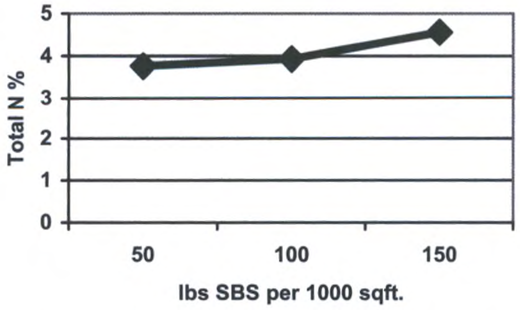
		Pre-Treatment	Post-Treatment	Time (weeks)						
				1	2	3	4	5	6	7
Ammonia (PPM)	Treated	127	0	0	5	8	15	19	20	18
	Control	119	119	125	125	138	114	128	98	97
Litter pH	Treated	8.5	1.7	2.1	3.4	4.5	5.0	5.5	5.9	6.4
	Control	8.9	8.9	8.7	9.1	8.5	9.3	8.6	8.1	8.9

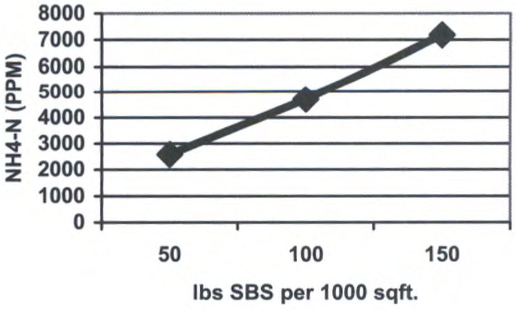
Current SBS Research in Poultry

A two-year NH_3 emissions study on a broiler farm in Georgia is currently being conducted by the Poultry Science and Biological & Agricultural Engineering Departments at the University of Georgia. Three of the broiler houses on a 6-house farm in Northeast Georgia are receiving PLT® litter acidifier at 50, 100, or 150 lbs. per 1000 sq ft over the entire area of the house (20,000 sq ft). Based on empirical calculations, 140, 280, and 420 lbs. of NH_3 should be bound per flock at the 50, 100, and 150 lbs. PLT per 1000 sq ft treatment levels, respectively. This farm averages 5.5 flocks per year.

House temperature, relative humidity and ventilation rates are being monitored by the computer controller in each house. The ventilation management is identical for each house regardless of treatment in order to simplify data analysis. Normally, ventilation rates would be adjusted based on ammonia and relative humidity levels in each house. A house with lower ambient ammonia levels would have reduced ventilation at a rate sufficient to maintain proper relative humidity within the house.

The initial experimental design called for the use of Dosi-tubes two days a week to establish a time weighted average as well as the use of Drager-Pac III electrochemical sensors to evaluate ammonia levels. Due to the lack of reliability of these sensors in a dry-litter broiler house, the rate of ammonia leaving the house is now being evaluated using the modified nitrogen mass-balance model (Carey, et al., 2005; Keener and Michel, 2005). Given that the amount of nitrogen entering the system (birds, feed, & sawdust litter) is identical for all three houses, increases in the amount of nitrogen retained in the litter are indicative of a decrease in the amount of ammonia being exhausted from the house. After 3 flocks, a linear increase is evident in both N and NH_4-N retained in the litter as the amount of PLT applied is increased (Fig. 2 & 3). The higher amounts of retained nitrogen in the litter of the 150-lb. treatment group, indicates a reduction in ammonia emissions in this house over the lower treatment rates based on the mass-balance model. Interestingly, total phosphorus levels were 20% lower in the 100 lb. & 150 lb. houses when compared to the 50 lb. house. The mechanism for the decrease in total phosphorus is unknown.





Figures 2 & 3. Amount of retained Total Nitrogen and NH4-N in broiler litter after three flocks of SBS usage on re-used litter.

Patterson, et al. (2006) recently completed a study in a high-rise commercial egg-layer facility to evaluate the use of PLT litter amendment for the reduction of ammonia and flies. PLT® was applied either at the rate of 0.97 kg/m^2 or 1.95 kg/m^2 on eight separate occasions during two 45-day experimental periods on a central row in the pit area of the house. A third row was left untreated as a control. Because layer manure does not contain a plant substrate, as does broiler litter, the moisture and ammonia content tend to be greater. Repeated applications of a litter amendment at higher rates are often necessary before significant changes in manure characteristics are observed. The same observations were made in this study where the higher rate of PLT showed the most consistent decrease in ammonia emissions (ppm/sec) with emission rates significantly lower than the control row on three out of the five sampling periods (0.2178, 0.8394, and 0.6435 for the high-treated vs. 0.6140, 0.9883, and 1.1863 for the controls respectively). Similar results were seen for the rate of Ammonia Linear Flux (mg/cm^2/min). As in the UGA study, manure ammonium (NH_4^+) nitrogen and P_2O_5 were positively altered by treatment group with the high-rate treatment group having the highest level of retained nitrogen and the lowest level of P_2O_5 (table 2).

Table 2. Commercial Layer Manure Analysis after 8 PLT® treatments over a 45-day period

Treatment	Total N (lbs/ton)	NH_4-N (lbs/ton)	Total Phosphate (P_2O_5) (lbs/ton)
Control	38.37^b	11.08^c	71.63^a
PLT-150	40.50^{ab}	13.75^b	62.38^b
PLT-300	46.08^a	17.06^a	55.48^c
P-value	0.0551	<0.0001	0.0004

Economics of SBS Use in Poultry

Multiple field demonstrations of PLT litter amendment use in commercial poultry complexes have also documented the economic benefits of using PLT® litter acidifier. Two field demonstrations completed in 1999 are discussed here.

A commercial broiler complex in the Southeast raising both a large (7.0 lb. or 3.2 kg) and small (4.5 lb. or 2.05 kg) bird evaluated the economic and performance benefits of using litter amendments from January – August 2000. Contract growers were given a choice of either using PLT® or an alum litter amendment (Al+Clear, General Chemical Corp., Parsippany, NJ) at the rate of 2.27 kg/9.29m^2 (50 lbs. /1000 sq ft) in the brood chamber (10,000 sq ft). Eighty-seven percent of the big bird growers and eighty-two percent of small bird growers chose PLT. The remaining thirteen percent of the big-bird and eighteen percent of the small-bird growers chose to use alum in an identical manner to the PLT. A total of 43.9 million birds were evaluated in this demonstration. There were no differences in housing or management between the treatment groups. Both the small and large bird groups raised on PLT substantially out performed the birds raised on alum (table3). In a complex of this size, the general rule of thumb used in the U.S. poultry industry is that an improvement in feed conversion of 0.01 lbs. of weight gain / lb. of feed consumption is worth $1 Million per year (Agrimetrics Associates, Inc., Midlothian, VA). The large birds raised on PLT had a feed conversion improved by 0.02 and the feed conversion of the small birds was improved by 0.04 over the birds raised on alum. This reduced performance shown by the birds raised on alum is consistent with production losses due to ammonia exposure reported in the literature (Miles, et al., 2004). This resulted in a net return of $2.7 million /yr over the cost of PLT ($305,000) on improved feed conversion alone in that complex. Additional economic benefit would have also been realized by the grower and the poultry integrator from the increases in weight and livability observed in this trial. The monetary return on investment observed would easily support an increased PLT application rate for the objective of ammonia emissions control. Similar results were achieved in another complex in the South-Central part of the U.S. where the same rate of PLT application was compared with untreated litter (table 4). The economic viability of the use of PLT for reducing ammonia emissions is the reason why so many poultry growers have voluntarily adopted this BMP.

Table 3. Production Data from Southeast Commercial Broiler Complex for all flocks raised on either SBS or alum from January-August 2000.

Bird Size	Performance Parameter	SBS	Alum
Large (7.0 lb/3.2 kg)	Total Number of Birds	19, 086, 816	2,846,212
	Livability (%)	88.86[1]	87.66
	Feed Conversion	2.27	2.29
	Weight (lbs)	6.92	6.81
	Condemnation (%)	1.77	2.11
Small (4.5 lb/2.05 kg)	Total Number of Birds	18,091,297	3,869,792
	Livability (%)	93.2	92.06
	Feed Conversion	2.05	2.09
	Weight (lbs)	4.52	4.5
	Condemnation (%)	1.07	1.99

[1] Includes Three flocks with livability <20% due to an ice storm and subsequent roof collapse

Table 4. Production data from South-Central Commercial Broiler Complex for all flocks raised on either SBS or untreated litter from October, 1999-March, 2000.

Performance Parameter	Untreated Control	SBS-Treated
Total Number of Birds Placed	9,101,579	9,921,203
Age (days)	40	39
Weight (lbs)	3.87	3.88
Livability (%)	96.73	96.84
Condemnation (%)	0.34	0.32
Feed Conversion	1.87	1.85

SBS Dairy

After the passage of California State Bill 700 and subsequent EPA Title V permitting of dairies in California, dairy farmers, particularly those in the San Joaquin Valley, began looking for practical and economical control technologies for VOCs and ammonia. Much effort has been spent on control technologies that deal with dairy slurry during storage such as solids separation and anaerobic digesters.

Ammonia losses from freshly excreted manures occur very rapidly and NH_3 conservation interventions need to be implemented within a few hours in order to be most effective (Meisinger, et al., 2001). Acidification of barn floors and gutters has been suggested as one possible intervention strategy (Ferguson, et al., 2001) but would require care in acid selection, as few liquid acids are compatible with the presence of animals. Acidification of manure slurry has also been suggested (Meisinger, et al., 2001; Clemens, et al., 2002; Lefcourt and Meisinger, 2001). Recent work by Frank Mitloehner, PhD (2005) at the University of California-Davis indicates that the majority of VOC emission occurs within hours after manure excretion prior to liquid manure storage as well. This new information requires a shift in focus to discover control technologies that can be applied to the free stalls or dry lots in the presence of cows. Sodium bisulfate was chosen for evaluation due to its efficacy in reducing ammonia levels and bacterial populations in equine and poultry bedding and its current use for environmental mastitis control in a few large Western dairies.

An experiment was conducted at the University of California - Davis by Frank Mitloehner, PhD to evaluate the efficacy of sodium bisulfate (Parlor Pal® bedding treatment, Jones-Hamilton Co, Walbridge, OH) surface application in reducing pH and ammonia emissions from dairy slurry at three different addition rates equal to 25, 50, 75 lbs. SBS/1000 Sq Ft compared to an untreated control. The EPA TO-15 VOC Panel was also measured. A 4x4 Latin square design was used with the 4 treatment levels and 4 cows. Urine and feces from each of the cows were blended on an "as excreted" basis and 2kg of each mixture were placed in a 4-inch high by 20-inch diameter well plate. pH readings were taken from 5 sites immediately pre and post SBS treatment. The well plate was then immediately placed in the emissions Flux Chamber for ammonia and TO-15 VOC evaluation. Ammonia and VOCs were evaluated at time 0, 24, 48 hrs and pH was measured again at 72 hrs. Three replicates were completed one week apart. Control and pre-treatment sample pH throughout the study ranged from pH 7.45 – 7.79. The 25, 50, & 75 lb. post treatment groups ranged from pH 2.98-4.16, 1.47-2.13, and 1.13-1.28 respectively. The variation seen in the 25 lb. treatment group is due to the difficulty in uniform surface application at the lower rate. Visual observations after SBS application include bubbles deep in the slurry and "leavening" of the slurry, which was increased at the higher application rates. This is most likely due to the interaction of SBS with carbonates in the slurry creating carbonic acid bubbles and the subsequent rise similar in action to a leavening agent. At 72 hrs, pH ranged from 7.68 – 9-00 with no real differences between treatments (Fig. 4). Ammonia flux was dramatically reduced immediately after SBS treatment with control flux ranging from 127.73 – 263.58 mg/hr/m^2 and all treated samples at 0 Flux (mg/hr/m^2).

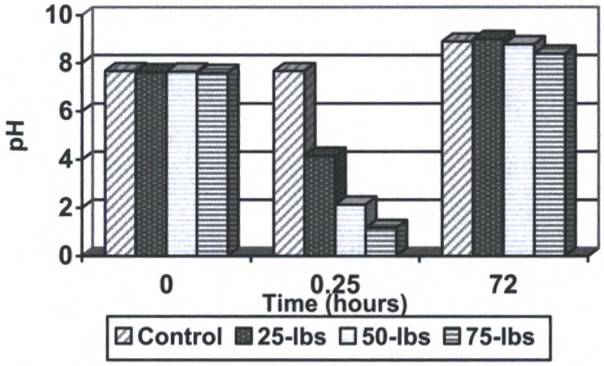


Figure 4. pH readings of dairy slurry treated with SBS (lbs/1000 sqft) over time.

Ammonia flux increased as time increased but there was always a linear decrease in NH_3 flux as treatment rate increased (Fig. 5-7). Most interestingly, NH_3 flux at 72 hrs was still substantively decreased over control even though pH levels between treatment groups were not significantly different and most were above a pH of 8.0. This indicates that the ammonia being produced by the slurry is being converted to and retained as ammonium sulfate and is not released as pH rises.

No changes in VOCs in the EPA TO-15 panel were noted. Even though this was the standard methodology at the time, the VOCs in the panel are unlikely to be produced by the bacterial degradation of animal manures. Subsequent work by Mitloehner (2006) has highlighted 5 oxygenated VOCs among others as the predominant VOCs produced by freshly excreted dairy manure. A similar study to the one outlined above is being repeated but with the dairy specific VOCs replacing the EPA TO-15 panel.

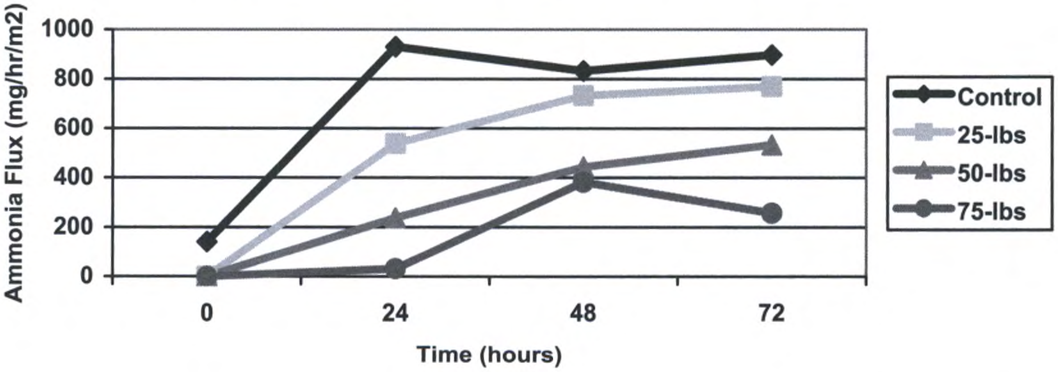


Figure 5. Week 1 Ammonia Flux (mg/hr/m^2) of dairy slurry treated with SBS (lbs/1000 sqft).

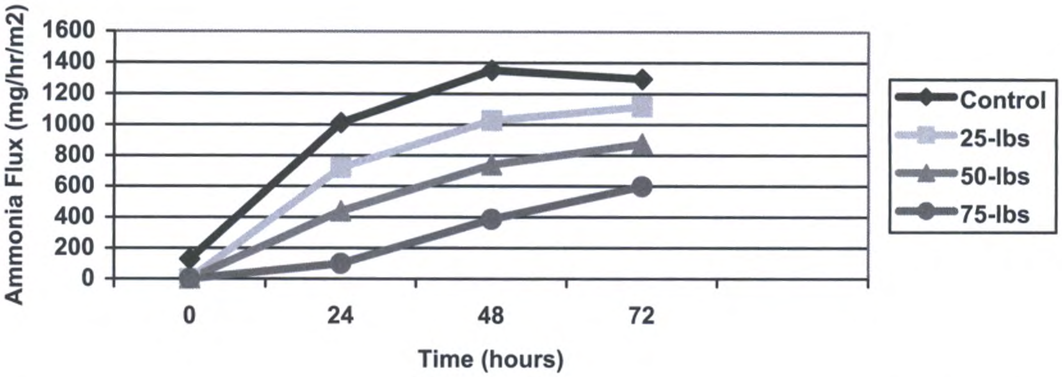


Figure 6. Week 2 Ammonia Flux (mg/hr/m^2) of dairy slurry treated with SBS (lbs/1000 sqft).

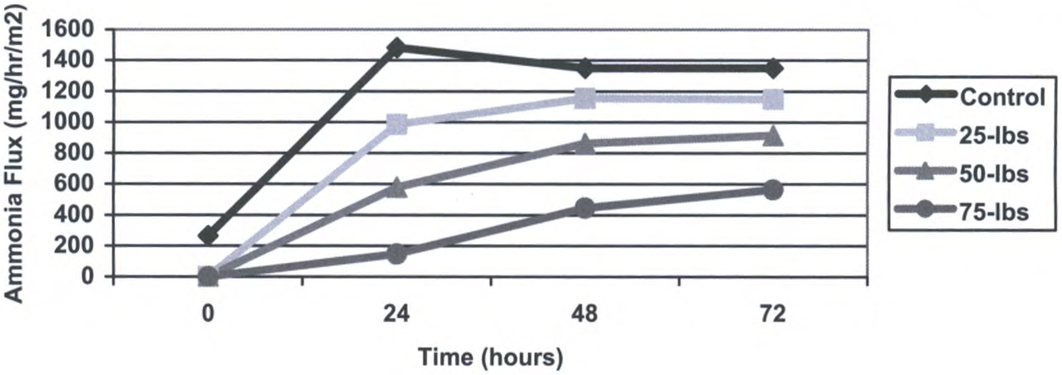


Figure 7. Week 3 Ammonia Flux (mg/hr/m^2) of dairy slurry treated with SBS (lbs/1000 sqft).

Summary

The use of sodium bisulfate as a best management practice for the reduction of ammonia and other gaseous emissions produced by the bacterial degradation of animal manures is well documented. The profitable economics of its use in commercial broiler operations is well recognized and has resulted in the voluntary adoption of this BMP by a substantial portion of the U.S. broiler industry. Its safety profile and the ability to apply SBS in the presence of animals should allow for the adaptation of this BMP to many other animal species.

Note: PLT® and ParlorPal® are registered trademarks of Jones-Hamilton Co., Walbridge, OH.

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Assessing the Impacts of Agricultural Biomass Burning on Visual Air Quality in Eastern Class I Areas Using a Multi-Sensor Approach

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Abstract

Data from satellite sensors such as the MODerate Resolution Imaging Spectroradiometer (MODIS) and ground based *in-situ* measurements have been analyzed to determine the impact of agricultural biomass burning on visual air quality in Eastern Class I areas. The combination of surface monitors from networks such as Interagency Monitoring for PROtected Visual Environments (IMPROVE) with time series and transport model analysis have been effective in determining sources of smoke to these sensitive areas. Products such as Aerosol Optical Depth (AOD), and ground based *in-situ* measurements such as Particulate Matter (PM) and visibility is examined. We expect that analysis of satellite data will lead to significant advances in the ability to discern sources of aerosol to these protective areas.

Introduction

Visibility is defined as "the greatest distance at which an observer can just see a black object viewed against the horizon sky"(Malm et al., 1999). A more general definition of visibility involves how well one can appreciate and differentiate colors, forms, and textures of an object from a distance. Visibility and regional haze are regulated in Class I areas such as national parks, national wilderness areas, and national monuments.

Particulates and gases that readily interfere with visibility originate from both anthropogenic and natural sources. Significant smoke events produced from large agricultural fires can have a profound effect on visual air quality. Ground based *in-situ* measurements and back trajectory receptor models are typically used to analyze visibility impacts. We show in this study that satellite data can also be useful in visibility-related studies. The ability of satellites to make observations over vast and remote areas make the data well suited for visibility studies. Satellites can provide a better understanding of pollutant sources and, potentially, aerosol concentrations in protected sites. This paper aims at using both *in-situ* measurements and spaceborne data to analyze visibility impairment to Eastern Class I areas. We particularly focus on recent agricultural burning episodes for 2005 in the Midwest and Central U.S to determine if smoke from these fires impacted visibility to Eastern Class I areas.

Methodology

Spaceborne data and *in-situ* ground based measurements were analyzed to determine possible smoke transport and its impact on visibility to Class I sites on the East coast.

Spaceborne and *In-situ* Techniques

Data from the MODerate Resolution Imaging Spectroradiometer (MODIS) instrument aboard the AQUA and TERRA satellites was used in this study. TERRA MODIS and AQUA MODIS view the surface of the entire earth every day. Data is acquired in 36 spectral bands, with up to 250m x 250m spatial resolution. Forty-four products are produced from the spectral data collected by the MODIS instrument. NASA provides MODIS satellite data in a format known as Hierarchical Data Format (HDF) (Kaufman & Tanre, 1998). The MODIS thermal anomalies product (MOD14) was used to identify occurrence and location of fires. MODIS thermal bands used to detect fires are collected at a spatial resolution of 1km. The product includes fire occurrence for both day and night, fire location, and energy calculation for each fire (Kaufman et al., 2003). MOD02QKM-Level 1B and MYD02QKM-Level 1B from the TERRA and AQUA platforms, respectively, were also used in the cases studied. This data was essential to produce quarter kilometer (QKM) resolution true color red-green-blue (RGB) images from the calibrated geolocated radiances.

MODIS Aerosol Optical Depth (AOD) product, MOD04, was also used. AOD measurements were used to determine the intensity of aerosols in the atmosphere.

The National Oceanic Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) (HYbrid Single-Particle Lagrangian Integrated Trajectory) HYSPLIT model was important to assess potential pollutant source directions (NOAA HYSPLIT, 2006). HYSPLIT computes the advection of a single pollutant particle or its trajectory. The online (Internet-based) HYSPLIT model was run using FNL archived meteorological data. Five-day air trajectories with start heights at 1, 2, and 3 km were produced to evaluate possible transport of smoke.

Data from IMPROVE aerosol fine particulate matter monitors were used, when available, to provide an understanding of chemical concentrations in the atmosphere. Environmental Protection Agency (EPA) Air Quality System (AQS) PM2.5 data was used in addition to IMPROVE aerosol data. Surface PM2.5 concentrations were also sourced from sites in EPA's Metropolitan Statistical Area (MSA). All of these particulate monitor measurements were useful to determine the quality of air at protected sites.

Results and Conclusion

The results of this study along with our conclusions will be presented at the conference proceedings. Please be sure to visit our poster.

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Operational Weather And Air Quality Forecasts For Fire Applications

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Abstract

The California and Nevada Smoke and Air Committee (CANSAC) forecast center is one of the five regional Fire Consortia for Advanced Modeling of Meteorology and Smoke (FCAMMS) and is located at the Desert Research Institute, Reno, NV. The main objective of the CANSAC operations is to provide accurate and high-resolution numerical weather and air quality forecasts to the region of California and Nevada to be used by the authorities in decision making for air quality and fire management issues.

In addition to main meteorological predictions, the center also generates smoke and fire danger assessment forecasts such as the National Fire Danger Rating System (NFDRS) and the BlueSky smoke prediction system, which predicts particulate matter ($PM_{2.5}$) impact from wildfires. Processed products of all the three types of forecasts are made available to the user on a public web page (cefa.dri.edu/COFF/coffframe.php) in visual and text formats. This study will describe the details of the CANSAC forecasts and their application areas.

Introduction

The California and Nevada Smoke and Air Committee (CANSAC) is a consortium of fire weather and air quality decision-makers, managers, meteorologists, and scientists in partnership to provide operational meteorological support for fire and smoke management, and advance the scientific understanding of atmosphere and fire interactions. CANSAC is one of the five regional Fire Consortia for Advanced Modeling of Meteorology and Smoke (FCAMMS) established as part of the National Fire Plan, and is dedicated to fire and smoke management in California and Nevada. The Desert Research Institute (DRI) Program for Climate, Ecosystem, and Fire Applications (CEFA) is the operational component of CANSAC and provides operational meteorological, fire assessment, and smoke forecasts as well as conducts research in order to improve fire weather and fire impact predictions.

The major goal of CANSAC is to link accurate and high-resolution weather predictions to fire and smoke impact in Nevada and California where nations largest fire incidents occur. In this perspective, CANSAC became operational in July 2004 and since then provided the users processed forecast products. These products include standard (e.g., temperatures, winds, humidity, precipitation) and diagnostic (e.g., vorticity, lifted index) meteorological elements and value-added information of smoke dispersion and transport and fire danger. A history of CANSAC and details describing the methods and techniques developed to compose a fully operational weather and smoke forecast system are given in Brown et al. (2003).

Real-time MM5 Forecasts

Operational meteorological forecasts are generated using the Fifth Generation Penn State/NCAR Mesoscale Model (MM5) (Grell et al., 1995) on a three-nested domain enclosing a greater area of the Western US and focusing on California and Nevada at a higher resolution. The domains consist of 97x97x32, 154x154x32, and 27x27x32 cells with 36, 12, and 4 km horizontal grid spacing for the outer, nested, and innermost domains, respectively (Fig. 1). The model is initialized twice daily (7 AM/PM PST) with North American Meso (NAM) model 00 and 12 UTC forecast outputs (Grid 212-40 km resolution). Observational initial conditions are obtained from Unidata LDM data stream. Physics options used in the model include the following schemes:

- Mellor-Yamada Planetary Boundary Layer (PBL) scheme
- Grell cumulus parameterization
- Simple ice moisture scheme
- Cloud radiation scheme

The model forecast lengths are 72-hrs for the two larger domains and 60-hrs for the California and Nevada domain (Fig. 1). Post-processing of the outputs is simultaneously performed as the model run continues and made available through the public CEFA web site (cefa.dri.edu/COFF/coffframe.php). Complete set of meteorological products includes the maps of upper air parameters (500, 850, 700 mb), surface parameters, precipitation, and fire weather indices. Soundings and meteograms of standard meteorological variables are given at selected 72 locations in California and Nevada. As the system develops, interactive GIS-based tools and products will be incorporated into the system.

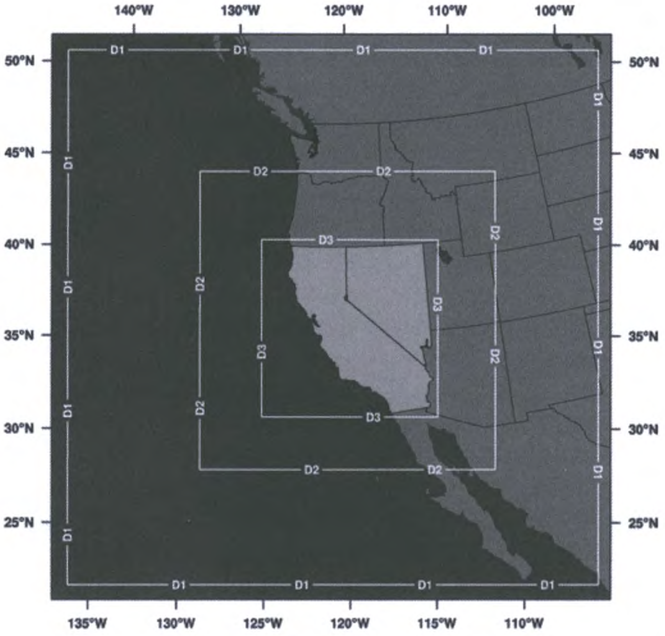
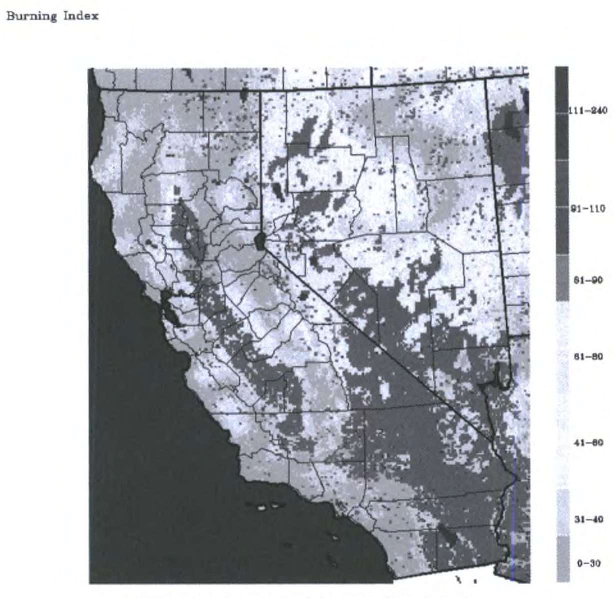


Figure 1. Three-nested domain of CANSAC MM5 forecasts. D1, D2, and D3 represent the borders of 36 km, 12 km, and 4 km grids, respectively.

National Fire Danger Rating System Forecasts

The National Fire Danger Rating System (NFDRS) was developed by the USDA Forest Service and is used by wildland fire management agencies in assessing the daily fire potential at local and regional levels. The system is extensively used and provides quantification of risk elements that are critical for daily decisions such as resource placement, appropriate suppression responses, and strategic decisions at local area to national levels. This method incorporates topography, fuels, and weather information in order to calculate day-to-day fire danger indices, which are composed of energy release component, spread component, burn index, and ignition component (Fig. 2). CANSAC provides gridded NFDRS maps for the registered users. These indices are calculated for the 12 and 4 km domains using meteorological fields derived from the MM5 forecasts at 00 UTC together with fuel information obtained from the USDA Forest Service.



GRAY represents agricultural, berren, and marsh areas

Figure 2. Gridded burning index map calculated for the CANSAC 4 km California and Nevada domain.

BlueSky Smoke Prediction System

BlueSky is a coupled modeling system to predict the smoke ($PM_{2.5}$) impact from wildland, agricultural, and prescribed burns. Developed by the USDA Forest Service AirFire Team in collaboration with land management and air quality regulator users, this system is comprised of a modeling framework combining emissions, meteorology, and dispersion models. The system requires input information of fire characteristics, meteorological conditions, and emissions to drive the dispersion and transport model. A detailed description of the BlueSky system is given by O'Neil et al. (2005).

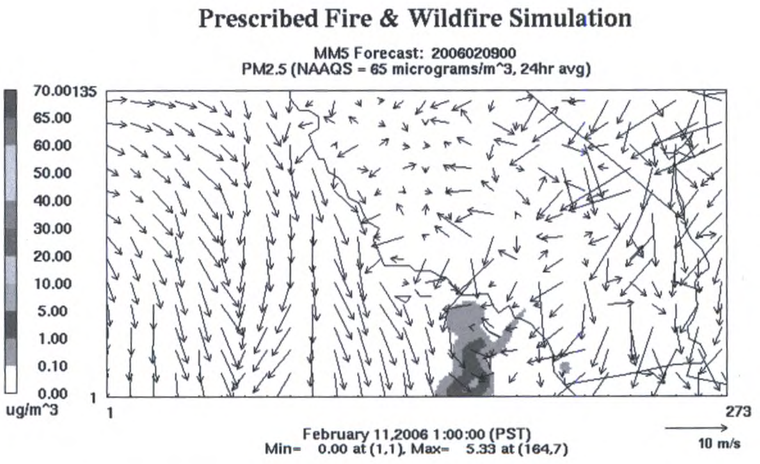


Figure 3. BlueSky $PM_{2.5}$ concentrations from a wildfire in southern California, 11 February 2006.

The BlueSky implementation adapted in CANSAC uses the 00 UTC MM5 forecast data and the fire emissions estimated based on the wildfire 209 reports to compute the $PM_{2.5}$ smoke dispersion and transport for the 12 and 4 km domains (Fig. 3).

Summary and Future Work

The CANSAC operational forecast system is a new dynamically developing system that involves multiple components with different input and output regimes. The current products have been compiled based on the user needs and will continue in developing with the same objective to improve the quality and usability. Evaluation of the each forecast component has not yet been completed and remains as the biggest pursuit of the near future plans.

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Photochemistry of Reservoir Species for Ozone-Destroying Halogens in the Stratosphere

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Abstract

The depletion of ozone in the Arctic and Antarctic due to reactions involving atmospheric chlorine has led to an explosion of interest in the chemistry of halogen oxides. ClO_x species, acting as a reservoir of chlorine, participate in catalytic reaction cycles that destroy ozone. Indeed, concentrations of ClO and OClO in the Antarctic stratosphere reach levels nearly two orders of magnitude higher than normal, and these levels are anticorrelated with measured levels of stratospheric ozone. Models of ozone depletion must account for the concentrations of chlorine oxides, the absorption cross-sections of these compounds, and the yield of free halogen due to the photolysis of these reservoir species. In addition, vibrationally excited species have proved to be important in atmospheric model calculations--*e.g.*, the "tropical O_3 deficit" at an altitude of 43 kilometers was resolved by considering the increased reactivity of vibrationally-excited O_2 species in the production of odd oxygen.[1]

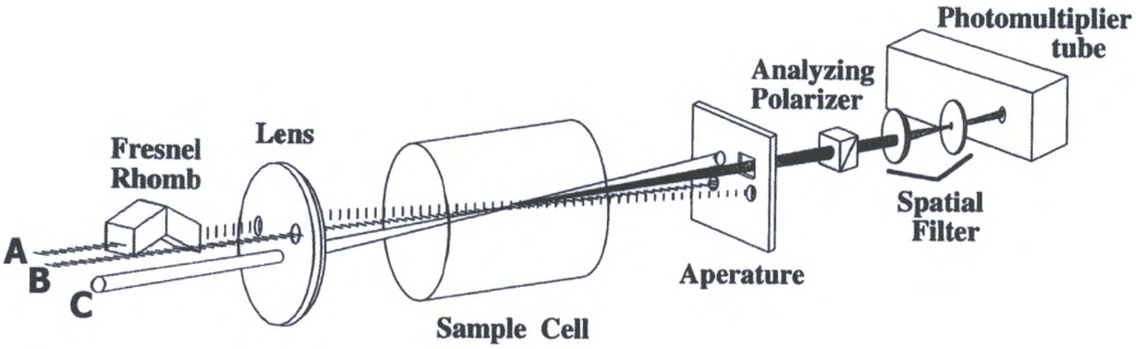
Photodissociation studies of small polyatomic molecules have opened the way to understanding two important aspects of reaction dynamics: selective bond fission and the breakdown of the Born-Oppenheimer approximation. The relationship between these two phenomena has manifested itself in studies of reaction dynamics on excited state potential energy surfaces that probe the importance of nonadiabatic interactions in influencing the branching ratio between energetically allowed product channels in molecular photodissociation. Many experiments examine the effect of curve crossings along the dissociation pathway by mapping the product internal state distributions or branching as a function of excitation energy. An alternative approach, which complements these methods and can probe the multidimensional nature of the coupling, involves examining the branching ratio as a function of the initial parent molecules' vibrational excitation.[2] These studies require the preparation of initial quantum states and a state selective detection of products, which can be achieved with modern laser technology.

For the case of predissociation, preparation of initial quantum states is possible by the excitation to well defined states in the upper electronic state. Reisler and coworkers[3] have demonstrated that parent ClNO bending is preferentially channeled into NO product rotational excitation, and studies of CH_3ONO photodissociation has shown that reactant NO stretching vibrations are preferentially deposited into product NO vibrations.[4] Hepburn *et. al.*[5] demonstrated that the electronic state distribution of the sulfur atom product from CS_2 photodissociation depends on which band in the $^1B_2$ absorption spectrum is pumped. These studies and many others demonstrate that selective excitation of well-defined vibrational levels in predissociative excited states may have profound effects on product rotational, vibrational, and electronic state distributions; however, there are few examples in which nuclear motion has been shown to have a strong affect on branching to chemically distinct channels. The predissociation of the reservoir species OClO following near-UV excitation is one of those few examples.

The absorption spectrum of OClO extends from 260 to 480 nm and is characterized by a long progression of vibronic transitions involving mainly pure symmetric stretch ν_1, with some neighboring bands involving ν_1 in combination with the bend ν_2 or with even quanta of the asymmetric stretch ν_3. The predissociative lifetimes are greater than 100 ps for the lowest-lying levels and shorten progressively with increasing energy to less than 1 ps. Near ultraviolet excitation of OClO results in primarily O–ClO fission to form O + ClO, a channel which leads to a net null cycle in the atmospheric ozone budget. However, a minor, concerted elimination channel, yielding Cl + O_2, leads to the net destruction of atmospheric ozone.[6] Davis and coworkers found that the photochemical yields of these two channels depend on the nature of the vibrational character of the excited state (e.g., a mode-specific photolysis).[7] For excitation between 380 and 475 nm, the Cl yield was slightly enhanced when combination bands containing one quantum of *bending* $(\nu_1,1,0)$ were excited and significantly diminished for transitions to OClO levels having *asymmetric stretching* $(\nu_1{-}1,0,2)$ character.

Competitive dissociation pathways in the photolysis of OClO can be attributed either to different electronically excited states involved in the transition, or to a single initially-prepared state that possesses two entirely different routes to these products. At photolysis energies above 3.1 eV (λ<400 nm), OClO is excited to the $A\ ^2A_2$ state and dissociates directly over a large potential energy barrier to form ClO + O. Below 3.1 eV, this first excited *A* state is bound with respect to direct dissociation and *indirect* dissociation mechanisms are operative. The *A* state intersects via spin orbit coupling a nearby $^2A_1$ state which is only weakly bound in the asymmetric stretch coordinate and dissociates to ClO + O via a nearly linear transition state. Calculations of Peterson and Werner[8] indicate that another dark state, the strongly-bent $^2B_2$ state, exhibits two transition states to dissociation. On the $^2B_2$ potential surface, Cl + O_2 can be produced via a transition state that is promoted by bending, and a second transition state leading to ClO + O can be accessed via the asymmetric stretching coordinate. Thus, nonadiabatic coupling of initially prepared *A* state to either different states ($^2A_1$ or $^2B_2$) or to two distinct regions of one state ($^2B_2$) yields branching ratios of products that are highly dependent on the nuclear motion of excited OClO.

We have preliminary evidence that the yield of Cl (the minor channel) also depends on the vibrational state of the parent molecule prior to photolysis. Even at stratospheric temperatures, an appreciable fraction of nascent OClO molecules populate vibrationally excited states and this contribution is neglected in current models. Transitions involving a vibrating OClO molecule access larger regions of the potential energy surface than transitions of a vibrationless ground state. These excursions can enhance the coupling to dissociative states and affect the branching between product channels. Unfortunately, the evidence of this enhancement is often buried beneath the more dominant spectroscopic signature of the vibrationless spectrum. Our multilaser experiments utilize a “tagging” scheme to isolate the role of parent bending or stretching motions on the photolysis of OClO. In these experiments the absorption spectrum of vibrationally "hot" molecules can be measured independent of the more abundant vibrationless species using a nonlinear spectroscopic technique—transient grating spectroscopy—involving three crossed laser fields.



Two of the three input laser beams are identical in frequency. At the crossing point of these beams the electric field is spatially-modulated due to the constructive and destructive interference of coherent radiation. This interference pattern is transferred to the sample when the frequency of this “pump” beam is tuned to an electronic transition of OClO. Transitions occur at the regions of constructive interference (fringes of the interference pattern) and *deplete* the population of ground state molecules in the sample. By choosing low-energy transitions to longer-lived excited states (>100 ps), this “tagging” scheme can select just a few precisely-defined initial states from the overall thermal population of states. When a third beam encounters the modulated population established by the pump beams, it is diffracted according to the depth of modulation and the strength of its resonance interaction with the sample. This “probe” beam is tuned to higher energy end of the predissociation region. Because the population of a select set of states is modulated, the diffracted signal reflects the absorption spectrum of only those states.

The influence of parent vibration on photolysis is exhibited in the lifetimes of predissociative excited states. We observe shorter lifetimes and thus enhanced nonadiabatic coupling for “hot band” transitions compared to “cold band” transitions. The maximum effect is a six-fold decrease in the lifetime of the predissociative state for transitions between ground bending states and pure symmetric stretching excited modes (0,1,0) →

(ν_1,0,0). This enhancement is less prominent for transitions to bending combination bands (ν_1,1,0) and asymmetric stretching combinations (ν_1,0,2); and least noticeable for transitions to a mixed combination band (ν_1,1,2).

Bromine, on the other hand, is found at much lower concentrations than chlorine in the polar stratosphere and far less is known about the BrO_x compounds. Nevertheless, model calculations suggest that bromine-catalyzed ozone loss could account for up to 40% of the total ozone depletion in the stratosphere because BrO_x catalytic cycles may be more efficient than the analogous ClO_x cycles. We will also describe our investigation of bromine production from the photolysis of OBrO. A theoretical study[9] of the low-lying excited states of OBrO indicate that a branching between BrO + O and Br + O_2 channels can once again be expected to depend on nonadiabatic coupling to nearby dissociative states. In 1991, methyl bromide was identified as a potential ozone depleting compound, and in 1992 it was officially added to the list of ozone depleting chemicals (Montreal Protocol). Although the oceans represent the largest known source of atmospheric MeBr, soil fumigation, biomass burning and production by plants, salt marshes, and fungi are also significant sources. Agricultural use of methyl bromide may be responsible for 3-10% of stratospheric ozone depletion.

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Ecosystems Organic Matter Management Problems and Modern Agricultural Biotechnologies Application in the Southeastern Ukraine

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Abstract

The main type of soil is chernozem or mollisol. Under current conditions the soil undergoes growing effects of human activities. The increasing of areas of agricultural land (especially arable) has led to the decreasing of areas of natural steppe, forests and other vegetation. The negative impact of industry and agriculture has led to environment degradation of ecosystems. Soil humus, commonly referred to as organic matter, represents an advanced stage in decomposition of organic material. In 1881 the humus content was 7.6 %. After 100 years, it was 5.5%, and in 1991 - 4.5%. During the last 30 years the content of humus in the soil has decreased by 10-70%. Annual losses of humus are 60 t/km^2. A significant correlation has been found between the amount of arable lands and humus content in the soils (R= 0.53). It was found that air pollutants caused significant damage to ecosystems.

Two factors - intensification and specialization were practiced in the collective farms during sixty-eighty years in the former USSR. For instance, 10-20 years ago the pig production complexes used 108,000 animal units. These created air, soil, water pollution problems due to excess manure. Now the pig industry uses livestock complexes with 5-10,000 up to 24,000 animal units. It is necessary to emphasis biogas is additional kind of fuel in Ukraine. There are several technologies on agro-waste utilization (biogas utilization, vermicomposting, etc), which are developed in Ukraine. The first one is technology of manure utilization to get methane. Several projects were developed. Dnipropetrovsk region takes first place in Ukraine on manure resources potential to produce biogas and manure slime as fertilizer. Second, the vermicomposting to transform manure and plant wastes has taken place in Ukraine the last decade. Humus substances from peat, brown coal, and lignite are additional examples of manufactured fertilizers, which are environmentally friendly. New bacterial fertilizers and biological control strategies include products, which are able to improve symbiotic and associative nitrogen fixation in the root zone.

Introduction

In the beginning of agrarian reform 70 % of total agricultural product (TAP) was produced by collective and state farms of Ukraine.30% of TAP provided the private sector. At present there exist collective, cooperative, individual and part-time personal subsistent farms. Today collective and private farms produce 38 and 2% of TAP respectively. The rest part of TAP is producing due to subsistent farms. A specific feature in the development of part-time subsidiary farms is that they enhance output without significant investment, credits, or funds from the state budget. Now such farms become principal commodity producers in the agricultural sector, making a considerable impact on the prices of basic foodstuffs. These farms produce now potato-98.6; other vegetables – 83.1; fruits and berries - 81.8; meat - 74; milk - 71; eggs-66.2; wool-61.4% (Melnik et.all., 2001). By the other words about one half of population in Ukraine is connected with agricultural production and trade. However these farms use a poor management to produce agricultural products. Consulting and extension services can help in information access to low input agri-technologies. Meantime the bases to provide sustainable agrarian potential are collective and private farms working in accordance with modern requests of market economy. Ensuring a sustainable total agricultural product is impossible without the agri-environmental policy implementation including biological land transformation, monitoring, restoration, to reserve areas for new parks and recreation zones creation (Kharytonov et all., 2002b). It is necessary also to develop new approaches in crops nutrition and agricultural wastes management to increase degraded soil biological activity.

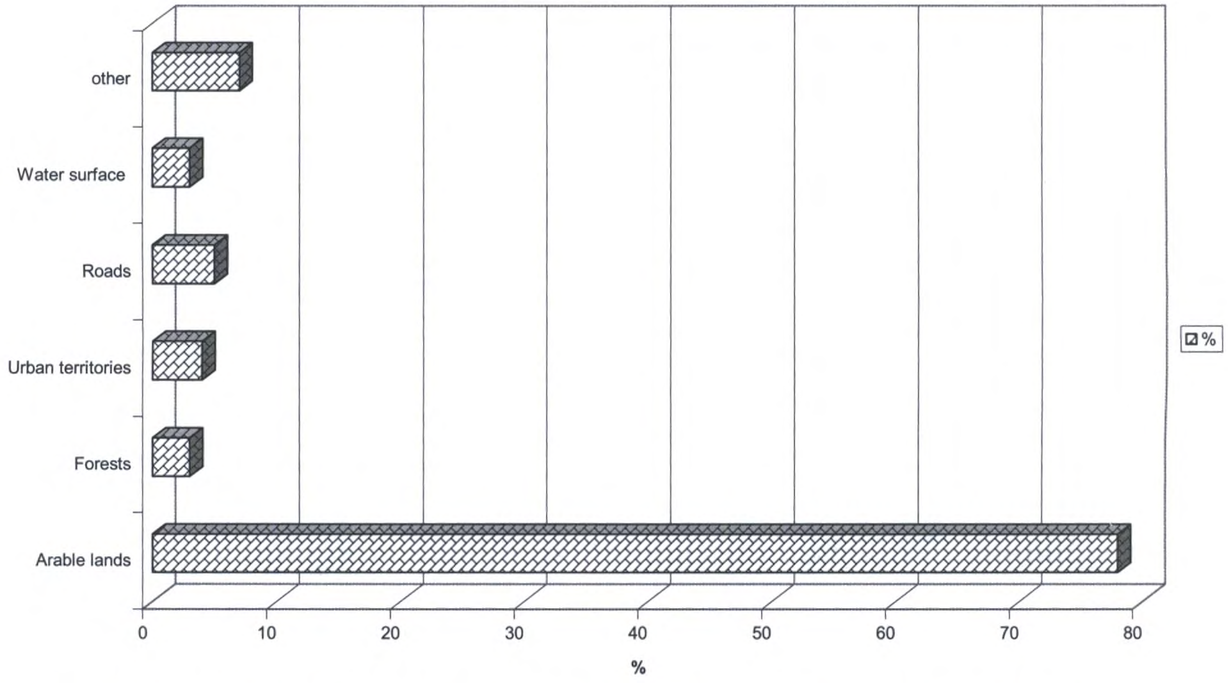
Methods

The investigations were conducted at rural and urban sites of the Region. Dnipropetrovsk Region (province) is situated in the southeastern part of Ukraine on both banks of the river Dniper and occupies an area of 31923 sq. km (5.3% of the total territory of Ukraine). The Region has 22 administrative districts (rural areas) and 13 municipalities. Natural resources formed the basis for leading industries of the economy at the national and regional level. Because of high level of soil fertility the great part of Dnipropetrovsk Region can be characterized as arable. The Region has more than 500 agricultural enterprises and about 2000 farms. The content of humus in the soils was determined by the relevant chemical-analytical method (Kharytonov et all., 2004). Some data portion were selected for the one farm to validate it for remote sensing application. Statistical methods were applied to describe quantitatively the relationships between soils components and some factors.

Results and Discussion

The land has been changing by man intensively. Human activities almost changed the landscapes of southeast Ukraine. Only 0.9% of Dnipropetrovsk Region area remains more or less natural. Because of the prevalence of highly fertile soils and favorable climatic conditions the average level of agricultural development of land is very high -79% - more than 25000 sq.km, but somewhere is reaches up to 90% (Fig. 1).

Fig.1. Structure of land stock in Dnipropetrovsk Region



The level of arable lands varies from 55% to 80%. On average there are 0.006sq.km of agricultural land and 0.005 sq.km of arable land per person in the Region (Ukrainian standard is 0.0015 sq.km per person).

The increasing of areas of agricultural land (especially arable) has led to the decreasing of areas of natural steppe, forests and other vegetation. But natural areas determine the stability of the biosphere, agricultural production, water exchange, cycle of substances, energy flow. For instance, in the steppe zone, to form the underground water flow and to protect the soil from erosion approximately of 10% of forests are required. But factual average forestry of the Region of 3-8% and the percentage of arable land should be decreased.

Due to location of the Region in the semiarid zone, the lands need to be irrigated. There are 2240 sq. km of irrigated lands in Dnipropetrovsk Region. It is 7.0% of the total area and 10.6% of the arable lands. The soil covering is extremely damaged by mining of mineral ores, black and brown coal. The total area of alienated land in the Region is about 340000sq.km - the highest amount in Ukraine.

In terms of level of land alienation, the mining industry is the main source.

There are several reasons to make changes in forests and agricultural lands distribution here. Main reason is connected with need to provide the biological conservation for washed soils, etc. A long-term degradation of the steppe grass ecosystems is also a part of the general process of environmental degradation in Ukraine. Unfortunately, erosion processes within steppe landscapes reach 40-50% in Ukraine. For instance the process of the washed soils formation in Dnipropetrovsk region increased dramatically for the last 33 years (Table 1).

Table 1. The soils erosion dynamic in the Dnipropetrovsky region for the last 33 years.

№	DISTRICT	Soils erosion dynamic		
		Thous.ha	% of total square	Δ(%)of total square
1	Apostolovsky	42,5	40,7	- 4.6
2	Vasilkovsky	57,3	48,9	+ 18.0
3	Verkhnedneprovsky	62,6	72,5	+ 20.8
4	Dnipropetrovsky	45,3	42,6	+ 2.3
5	Krivorozhsky	49,0	47,5	+1.3
6	Krinichansky	81,5	54,3	+ 3.2
7	Magdalinovsky	16,6	12,0	+ 0.3
8	Mezhevskoy	48,1	42,8	+ 21.1
9	Nikopolsky	74,0	55,4	+12.0
10	Novomoskovsky	44,3	30,0	+ 7.0
11	Pavlogradsky	41,7	37,1	+10.7
12	Petropavlovsky	52,2	47,9	-3.0
13	Petrikovsky	1,8	3,3	-
14	Pokrovsky	43,1	40,8	+ 18.2
15	Pyatikhatsky	70,3	48,4	+ 7.5
16	Sinelnikovsky	77,4	53,4	+ 6.5
17	Solonyansky	87,5	56,8	+ 0.5
18	Sofievsky	56,2	46,2	+ 3.2
19	Tomakovsky	50,3	52,8	+ 4.2
20	Tsarichansky	3,1	4,2	0.0
21	Shirokovsky	37,1	38,3	- 4.9
22	Yurievsky	41,7	52,5	-

There is more than 43,5% from the total territory of eroded land in the Region. High level of the soils erosion dynamic for some districts is connected with intensive agriculture development in spit of non favorable landscapes conditions. This increase in erosion has accelerated during the process of agricultural reform that began at Ukrainian independence in 1991. Collective farms have not had the money to invest in erosion control, even though they have the technical experience to fight erosion effectively. Private commercial farms often have little incentive for soil conservation since they rent most of the land they farm from others, without long-term commitments. Since independence, subsistence farmers have produced a large amount of the total agricultural product (60% in 1998). They often lack capital, machinery or technical awareness to effectively combat erosion, and may lack motivation if they are using a specific plot only temporarily (Kharytonov et al., 2002b).

Thus land use planning demands increasing attention. Nature protects the land by covering it with vegetation. More interchange and adaptation should take place between the space design orientation of the resource planner.

The most important property of soil is its fertility. The main type of steppe soils is chernozem or mollisoil. In the USDA system, chernozems fall into the broad grouping of mollisols www.fao.org/DOCREP/003/Y1899E/y1899e15.htm).Under current conditions the soil undergoes growing effects of human activities. The increasing of areas of agricultural land (especially arable) has led to the decreasing of areas of natural steppe, forests and other vegetation. But natural areas determine the stability of the biosphere, agricultural production, water exchange, cycle of substances, energy flow. Ukraine natural zones consist of three zones – forest, forest - steppe and steppe zone. Many years of little precipitation (350-500mm) were the main reason to consider the steppe zone of Ukraine as a zone of risky agriculture. At the same time the negative impact of industry and agriculture has led to environment degradation of ecosystems. The soil covering is extremely damaged by mining of mineral ores and black and brown coal. In terms of level alienation, the mining industry is the main source. One of the most important properties of black soil is high content of humus (up to 5.3%). Soil humus, commonly referred to as organic matter, represents an advanced stage in decomposition of organic material. Long extensive exploitation of mollisols, use of heavy agricultural machines, application of fertilizers and pesticides, influence of industrial and agricultural pollution have affected the soil properties and soil forming process, potential fertility and brings down the production and nutrition worth of agricultural products. In 1881 the humus content was 7.6 %. After 100 years, it was 5.5%, and in 1991 - 4.5%. During the last 30 years the content of humus in the soil has decreased by 10-70%. Annual losses of humus are 60 t/km^2. A significant correlation has been found between the amount of arable lands and humus content in the soils (R = 0.53). There was no correlation between humus content in the soils (R = 0.11). Modern remote sensing approaches were applied to check humus content for selected collective farm of Sinelnikovsky District (Voloshyn et all., 2005).

The level and character of air pollution depend on different reasons: type, quantity and quality of industrial emissions, type and intensity of physical and chemical atmospheric processes, land surface etc (Babiy A.P., 2003; Kharytonov M.M., 2002a). Some plant and soil animal reactions depending on air pollution were assessed statistically too (Table 2).

Table 2.Some plant and soil animal reactions relations depending on air pollution

№	X	Y	Regression equations
1	Peroxidase activity in leaves	Atmosphere dust, mg/m^3	$y = -12.5x^2 + 7.3x + 3.0$
2	Chlorophyl content in leaves, mg/g	Atmosphere dust, mg/m^3	$y = 13.6x^2 - 7.4x + 4.1$
3	Death cases in seed embryos	Atmosphere dust, mg/m^3	$y = 66.2 \cdot x^{0.2}$
4	Chromosomes aberrations, %	Atmosphere dust, mg/m^3	$y = 2.4 \cdot 364.8^x$
5	Soil animals quantity per sq.m	NxOx in atmosphere, mg/m^3	$y = -434407x + 24140.7$

More dramatically negative emissions impact was established for the two indexes: chromosomes aberration in leaves and soil animals' quantity. An average percentage of chromosome aberrations in the leaves samples taken in some contaminated sectors of was more than 20-30 times low comparative to control. Soils animals' quantity decreased on 78% regarding to control. Thus it is obviously that air pollutants caused significant damage to ecosystems. That is why the forecasts on ecosystem buffer capacity for some emissions are actually.

Meantime two factors - intensification and specialization were practiced in the collective farms during sixty-eighty years in the former USSR. For instance, 10-20 years ago the pig production complexes used 108,000 animal units. These created air, soil, water pollution problems due to excess manure. Now the pig industry uses livestock complexes with 5-10,000 up to 24,000 animal units. It is necessary to emphasis biogas is additional kind of fuel in Ukraine. There are several technologies design on agro-waste utilization (biogas utilization, vermicomposting, etc), which were developed in Ukraine. The first one is technology of manure utilization to get methane. Several projects were developed. Dnipropetrovsk region takes first place in Ukraine on manure resources potential to produce biogas and manure slime as fertilizer (Kharytonov M., 1999). Second, the vermicomposting to transform manure and plant wastes has taken place in Ukraine the last decade (Kharytonov et al., 2000). Humus substances from peat, brown coal, and lignite are additional examples of manufactured fertilizers, which are environmentally friendly (Kharytonov , 2005). New bacterial fertilizers and biological control strategies include products, which are able to improve symbiotic and associative nitrogen fixation in the root zone (Kharytonov , 2002b).

Conclusions

Ensuring a sustainable total agricultural product is impossible without the agri-environmental policy implementation including biological land transformation, monitoring, restoration, to reserve areas for new parks and recreation zones creation. It is necessary also to incorporate the usage of ecological farming elements including modern agricultural wastes management.

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Chemical Composition of PM10 at an Agricultural Site on the Outskirts of Delhi, India

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Abstract:

World health Organization (WHO) once rated Delhi as the fourth most polluted city in the world. The concentration of PM10 in Delhi exceeds by many times the national and WHO standards resulting in adverse effects on human health and visibility in the area. The main sources of PM10 in Delhi are vehicular and industrial emission. However, agricultural and domestic sources also contribute significantly at the localized levels. The present study was undertaken to determine the concentrations of SO4, NO3, NH4, OC and EC in PM10 at an agricultural site in the outskirts of Delhi. The concentrations were compared with those at non-agricultural site also in the outskirts of Delhi. The study was carried out during a period of June- October 2003. The period includes pre-monsoon and post- monsoon months in Delhi. Sampling of PM10 was done by Anderson cascade impactor simultaneously at both the sites. In general the concentration of PM10 was more in pre and post monsoon months as compared to monsoon months and it was highest in the month of June when heavy dust storm conditions prevail. The average PM10 concentration-175 µg/m3- was about three times higher than the national standard value of 60 µg/m3. The concentrations of NH4 and EC were significantly high at the agricultural site as compared to nonagricultural site indicating thereby the influence of livestock and biomass burning activities on the air quality of the area. Considering a large number of farmhouses and dairy animals in and around Delhi, systematic expansion of the study is urgently required so that effective steps for agricultural emission regulation can be taken.

Introduction

Much of the concern about air pollution is focused on industrial and urban sources. However, air pollution from agricultural activities contribute significantly to air pollutants, it has been a neglected area. Agriculture comprises many types of activities, from crop production to raising animals for food animal agriculture, and related activities. It is one of the major sources of air pollution worldwide. Agricultural activities contribute directly to emissions of air pollutants through a variety of processes: enteric fermentation in domestic livestock (i.e., methane gas produced during digestion), manure management, rice cultivation, agricultural soil management, machines used in agricultural operation (diesel irrigation pumps) and burning of agricultural residues. Animal feeding operations (AFOs) are a source of a number of air pollutants of concern, including particulate matter (PM), ammonia, hydrogen sulfide, greenhouse gases (e.g., methane and nitrous oxide), odor, and volatile organic compounds. In large enough concentrations, these pollutants can cause adverse human health or ecological effects.

Delhi, the capital city of India, is one of the 10 most polluted cities of the world (Aneja et al., 2001). Major air quality concern in India is suspended particulate matter (SPM) and respirable particulate matter (RSPM) (Bhanarkar et al., 2002) affecting human health and visibility in the area. While generally the interest of international development research and funding agencies in urban and peri-urban agriculture is increasing very little work has been done in India.

Site Description

Delhi is situated 160 Km south of the Himalayas (28°21'17" to 28°53' latitude and 76°20'37" to 77°20'37" longitude) at an altitude of between 213.3 and 305.4 m above mean sea level. It is surrounded by the Thar Desert of Rajasthan in its west and hot plains of central India in its south. The study site, Natthupura is a village in the outskirts of Delhi with agricultural activities. Due to the rapid urbanization agricultural activities are limited to the outskirts of metro cities like Delhi.

Sampling

Sampling was done at two sites viz. one agricultural sites in outskirts of Delhi and another non-agricultural site, during a period of June-October 2003. The period includes pre-monsoon and post-monsoon months in Delhi. Samples were collected over 60-80 h sampling periods using an eight-stage Andersen impactor (Andersen Instruments Inc., USA). The impactor has 50% cut-off aerodynamic diameters of 10, 9, 5.8, 4.7, 3.3, 2.1, 1.1, 0.65 µm for stages 1-8, respectively, and collects all particles smaller than 0.43 µm on an after-filter. Flow rate was maintained at 28.1 Lt/m. Glass fiber filters (Schleicher and Schull, Germany) were used as collection substrate and were kept in dessicator after sampling.

Analysis

Anion concentration was measured by spectrophotometer by following standard methods. OC and EC were quantified by thermographic method using ELTRA CS-500 carbon analyzer.

Result and Discussion

Average concentrations of SO_4, NO_3, NH_4, OC, EC and PM_{10} were found to be 10.59, 4.54, 12.61, 59.05, 24.40 and 175.00 $\mu g/m^3$ respectively. PM_{10} concentration is about three times higher than the national standard value of 60 $\mu g/m^3$. As this site is located upwind to the city, it might affect the air quality of downwind region. The concentrations of NH_4 and EC were found to be higher at the agricultural site as compared to nonagricultural site. Ammonia is produced more in areas with intensive livestock and agricultural activity (TERI, 2001). This could be the reason for higher NH_4 concentration at Ntthupura while prevalent use of biomass burning and use of cow dung cake and kerosene as a fuel for auxiliary household work could be responsible for the higher values of carbonaceous aerosols. Considering a large number of farmhouses and dairy animals in and around Delhi, systemic expansion of the study is urgently required so that effective steps for agricultural emission regulation can be taken.

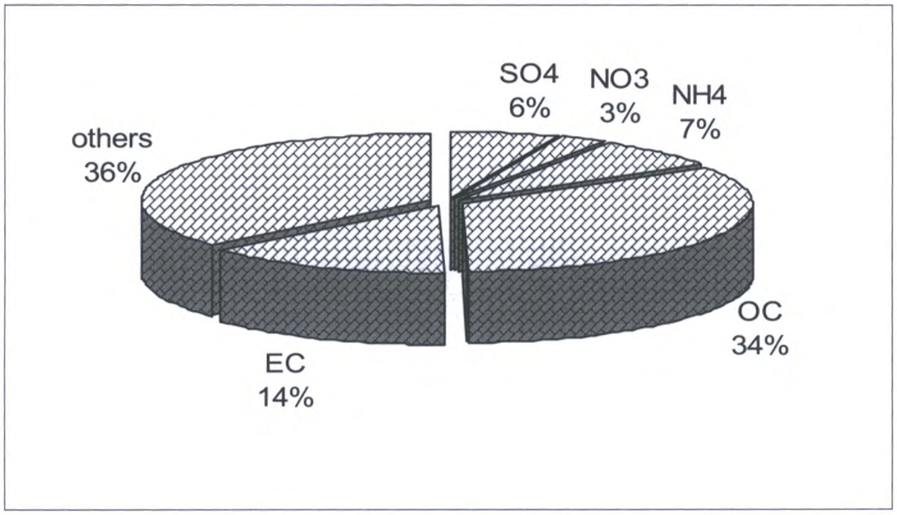

Figure 1. Percentage of analysed species in PM10 at Natthupura

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Measurements of N_2O Emissions from Agricultural Soil in Southwestern Korea

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Abstract

A closed flux chamber system was used for measuring nitrous oxide (N_2O) emission both from agricultural soils and at Kunsan, port city in the southwestern Korea. In temperate agricultural soils, its increasing emissions and concentrations are largely associated with agricultural activities such as use of fertilizer. These are also possible to increase nutrition into down flow area such as estuary, and thus to tidal flat. In order to elucidate characteristics of soil nitrogen emissions from agricultural, N_2O soil emissions were measured at every hour during the experimental period. Soil parameters (moisture, temperature, pH and soil nitrogen) were also measured at the sampling plots. Base on agricultural soil emission data, monthly averaged N_2O fluxes during May, June, and July were 0.14±0.08, 0.05±0.03, and 0.13±0.06 mg-N_2O $m^{-2}h^{-1}$, respectively. While soil temperature and soil pH do not seem to vary significantly over the experimental period, soil moisture varied significantly from 32% to 56% in WFPS in agricultural soils. Strong positive correlation (R^2= 0.57, $P < 0.0001$) was found between N_2O flux and soil moisture. Soil N_2O emissions from rice paddy soils were relatively lower than those from upland soils; anoxic condition due to saturation could limit the gas productions by producing nitrate reduction. Contribution from agricultural soil to the national N_2O emission should be not neglected in estimation estimating the national emission inventory.

Introduction

In the lower atmosphere, total oxides of nitrogen (NO_y) have been recognized as important chemicals because of their strong oxidizing capabilities and central roles in controlling ozone related chemistry (Crutzen 1979, Penkett 1988). Nitrous oxide (N_2O) is an important trace gas because it is a long lived greenhouse gas and the major source of stratospheric NO (Cicerone, 1989). The global warming potential of N_2O is about 250 times greater than each molecule of CO_2. N_2O currently accounts for 2-4% of total global warming potential (GWP) (Watson et al., 1992) and could be as much as 10% contribution of GWP in the future (Dickinson and Cicerone, 1986). Based on an IPCC report, the soil is a dominant source of atmospheric N_2O, contributing about 57% (9 Tg y^{-1}) of the total annual global emission. Mosier et al. (1998) reported that most atmospheric N_2O is of biogenic origin and produced by bacteria in soils. N_2O concentrations have been increasing rapidly for a number of decades. Their increasing emissions and concentrations are largely associated with agricultural activities (Xing 1998, Kroeze et al. 1999). Wet tropical forests have been recognized as a relatively high N_2O emission area because there is a high rate of nitrogen turnover. Cultivated land is now estimated to be an even larger source than the wet tropical forests attributing to the use of synthetic nitrogen fertilizers (Prather et al. 1995, Cole et al. 1996). Fertilizers can also significantly increase NO and N_2O emissions, via deposition of volatilized ammonia on natural ecosystems and denitrification of leached nitrate in sub-soils, surface and ground waters and sediment (Cole et al. 1996). Although it is now understood that agricultural soil is a significant source of N_2O, the quantification of these gas emissions from soil is difficult because of their large spatial and temporal variability (Kroeze and Mosier 2000, Kim et al. 2002).

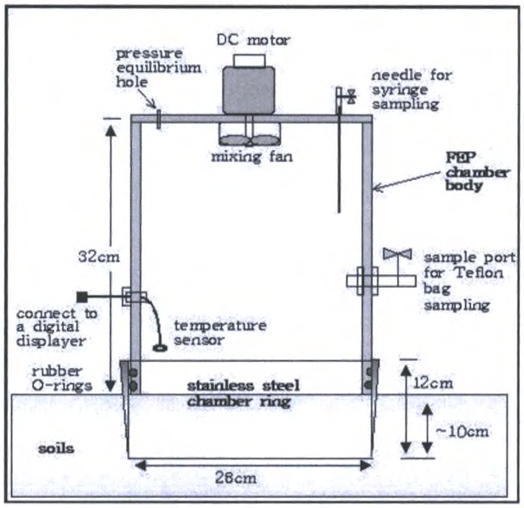
The southwestern coastal plain in Korea is the most intensively cultivated area. Rice cultivating area in the plain accounts for ~34% of the total cultivated area in Korea and contributes ~35% of the total annual national rice production. Agricultural activities in this area have been intensifying over recent decades; in particular there has been increased use of nitrogen and/or ammonium fertilizer for high crop yield efficiency. It could be suspected that this increase in use of nitrogen fertilizer will escalate soil nitrogen emission over this area and also to the near estuarine area. Measurements of GHG emission from the estuary and tideland in this area has being conducted.

The primary research of this study was to measure N_2O flux from intensively managed agricultural fields at Kunsan (port city located in the southwestern plain of Korea) and estimate the local nitrogen flux from agricultural soils. Results from different fields were compared. The knowledge from these experiments will help improving model study to estimate biogenic nitrogen soil emissions in Korea, and make us understand the role of soil nitrogen emission in local and global atmospheric chemistry.

Methods

Two agricultural experimental sites (upland and rice paddy) have been chosen to conduct flux experiment. Agricultural sites were located in the city of Kunsan (126.72°E, 35.95°N), Korea. The upland site is a private farm on which sesame and green perilla were cultivated; and the rice paddy site is managed by the National Honam Agricultural Experiment Station (NHAES) for the national greenhouse gas (GHG) emission research. Total area of the experimental upland site is about 2,000 m^2; about 50% of the total area was planted with sesame, and the rest of the area was planted with green perilla. At the upland field, about 2 kg of barnyard manure was applied two weeks before the measurement. The rice paddy field at NHAES was flooded during the measurement period, and water depth in the rice paddy was about 7 cm above ground surface. The average height of rice plants during the measurement was about 20 cm.

Figure 1. Schematic of closed flux chamber system



Daily soil flux measurements were conducted by using closed chamber technique. The enclosure consists of two parts, a stainless steel ring and a chamber body. The chamber is made of a fluorinated ethylene propylene (FEP) cylinder (diameter ~28 cm, height ~32 cm, and volume ~20 l). Figure 1 shows the flux chamber. The stainless steel ring was inserted into the sampling plot during a previous night of the measurement day. This minimizes the artificial effect on situ gas flux measurements due to soil disturbance by inserting a whole chamber into the soil just before the measurement (Kim et al. 2002). Hourly flux measurements were completed during non rainy days from May to July 2002 between 8:00 and 18:00 local standard time. About 60% data from the total experimental time was collected. Total of 21 days measurements were conducted from the experimental plots and analyzed soil characteristics such as soil pH, soil moisture and total Kjeldahl nitrogen. A soil was sampled from the center of the chamber footprint at the end of the experimental day. In order to measure a gas flux from the surface covered by the enclosure, air inside chamber was collected three times every 15 minutes by plastic syringes right after placing the chamber body onto the chamber ring. The volume of air sample was 50 ml for N_2O analysis by GC-ECD (gas chromatography with an electron capture detector). Each gas sample in the syringe was analyzed for five replicates by the GC, and the average N_2O concentration from the replicates was used for the calculation. The soil gas flux was calculated by the following formula derived from mass balance in the chamber (Kim et al. 2002).

$$J_{gas} = \rho_{gas} \times V/A \times \Delta C/\Delta t \times 273/(273+T)$$

where, J_{gas} is soil gas emissions, ρ_{gas} is gas density, V is chamber volume, A is the covered area by the chamber, T is average temperature inside the chamber during the 15 minutes sampling time interval, and $\Delta C/\Delta t$ is the rate of gas concentration increases with sampling time interval.

Results and Discussion

During the experimental periods, average N_2O flux from the experimental plot was 0.10±0.07 mg-N_2O m^{-2} h^{-1} over the period. The N_2O emissions range from 0.01 to 0.25 mg-N_2O m^{-2} h^{-1}. On monthly base, minimum average N_2O emission, 0.05±0.03 mg-N_2O m^{-2} h^{-1}, was recorded in June and maximum in May was 0.14±0.08 mg-N_2O m^{-2} h^{-1} after side-dressing of the fertilizer. These results seem to be comparable to the values reported from a cone field at the Lower Coastal Plain in North Carolina (Roelle et al., 1999). Soil N_2O emissions and soil characteristics from the agricultural fields were summarized in Table 1.

Table 1. Summaries of means of N_2O fluxes and soil characteristics

Month	mg-N_2O/m^2/hr	WFPS (%)	Soil Temp (°C)	pH	T-N (%)	NO_3^-	NH_4^+	TOC (%)	Rain fall (mm)	No. of day
May	0.14	48.6	12.9	4.75	0.21	18.4	3.24	3.47	137.6	6
June	0.05	37.8	13	4.56	0.19	28.7	2.10	3.11	68.8	6
July	0.13	46.9	14	4.58	0.19	25.5	1.06	2.68	316.2	9
Paddy†	0.03	flood	NM‡	6.98	0.21	NM‡	NM‡	2.49	NM‡	2

†Rice paddy soil measurements for 2 days during June 2000, NM‡ indicates no measurement.

If comparing these N_2O fluxes to those from rice paddy field, relatively low amounts of N_2O flux from the paddy soils were found. It could be due to the presence of water level over the paddy field. The flooded water could prevent gas from releasing from the paddy soil. It has been known that soil parameters (i.e., moisture, pH and N contents) have strongly correlated to the soil N_2O emissions; however, there are many uncertainties in the direct relationship between these parameters and soil emission. Precipitation data revealed that relatively dry soil condition consisted during June comparing to other months. Results in Table 1 indicate that N_2O flux from the June was the minimum. The shortage of moisture owing to dry soil could reduce microbial activities in the soil, and thus result in low N_2O gas emission under the dry soil condition. The correlation between N_2O soil emission and other parameters were shown in Figure 2.

During the experimental periods, all of the soil parameters, except NO_3^--N, have positive relationship with soil N_2O flux (Figure 2). There was a strong positive relationship between soil moisture (in WFPS%) and soil flux, and statistically significant (R^2=0.57, P<0.0001). Soil temperature values varied from 8.4°C to 16.4°C and monthly averages were recorded 13°C in June and 14°C in July during the measurement period. Presence of optimum soil temperature and moisture ranges for soil gas emission has been reported in previous researches (Davidson, 1991; Sadd and Conrad, 1993). Relatively weak positive relationship between the flux and soil temperature, in our experiment, was observed (R^2=0.17, P=0.0599). In certain range of pH values, Soil N_2O flux also increased as soil pH increases. Simek et al. (2002) reported that production of NO and N_2O gases from soil was high in range of soil pH from 6.5 to 7.5. The soil pH from the experimental plots were shown pH 4.4~pH5.0, which were acidic during the experiment. Release of H^+ into soil through nitrification relating soil aerobic microbial process should affect increase the soil acidity. Mean of total nitrogen was not varied significantly during the measurement, and soil amounts of NH_4^+-N were measured one order of magnitude lower than those in soil NO_3^--N (Table 1). Barnyard manure (containing more ammonium form than nitrate) was applied over the site surface, and NH_4^+-N could more easily release in the form of NH_3 from the soil surface. It appears that low levels in soil NH_4^+-N may be due to NH_3 volatilization and runoff by precipitation during the experiment. The negative relationship between soil NO_3^--N and N_2O flux in Figure 2 may suggest N_2O produce in the process of denitrification (NO_3^- convert into N_2).

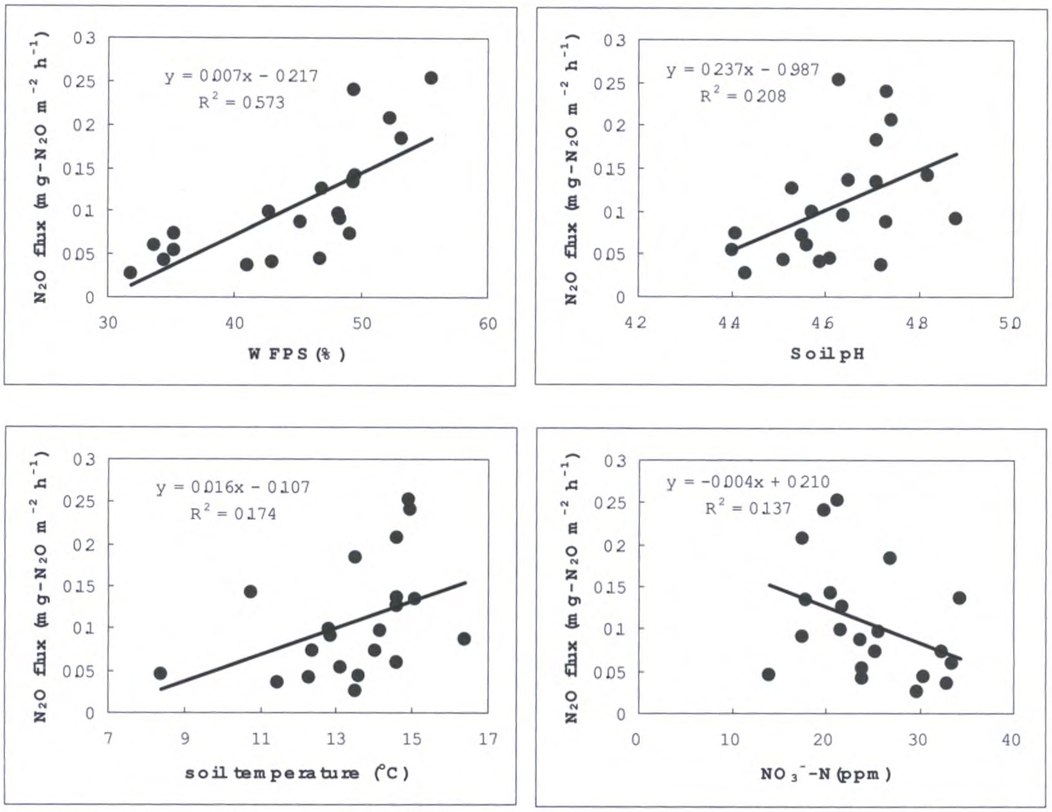


Figure 2. Relationship between soil N_2O flux and soil parameters during the experimental period

Conclusions

In temperate agricultural soils, increase nitrogen in soil emissions is largely associated with agricultural activities such as use of fertilization with urea or ammonium. These are also possible to increase nutrition into the estuarine area by transport and deposition. In order to understand characteristics of soil nitrogen emissions from agricultural soils, hourly N_2O soil emissions were measured and compare in terms of soil parameters during the growing season. Soil parameters (moisture, temperature, pH and soil nitrogen) were also measured at different soil characteristics, upland agricultural and rice paddy soil in Korea. While soil temperature and soil pH do not seem to vary significantly over the experimental period, soil moisture varied significantly from 32% to 56% in WFPS in agricultural soils. Strong positive correlation was found between N_2O flux and soil moisture. Soil N_2O emissions from rice paddy were significantly lower than those from upland soils; anoxic condition due to flooded water could restrict surface release of N_2O by producing nitrate reduction. It could suggest that contribution from agricultural soil to the national N_2O emission would be important. Even from the flooded paddy field, there was sufficient N_2O emission was detected. N_2O fluxes from agricultural soils need to be taken into account in estimating the national emission inventory.

Acknowledgement

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Trends in Agricultural Ammonia Emissions and Ammonium Concentrations in Precipitation over the Southeast and Midwest United States

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Abstract

Emissions from agricultural activities, both crop and animal, are known to contain gaseous ammonia (NH_3) which through chemical reaction changes into ammonium ion (NH_4^+) in the atmosphere. Using wet deposition data of ammonium from several National Atmospheric Deposition Program/National Trends Network (NADP/NTN) and Clean Air Status Trends Network (CASTNet) sites as well as calculated ammonia emissions from North Carolina and the Southeast and Midwest regions of the United States, trends in ammonium concentrations in precipitation were analyzed for the period of 1983-2004. The beginning of 1997 coincides with the implementation of a swine population moratorium in the state of North Carolina. Results from the analysis in North Carolina indicate decrease of positive trends in $NH4^+$ concentration in precipitation since the moratorium was placed into effect. Sampson County, NC, saw stable ammonium ion concentrations from 1983-1989, an average rise of 9.5% from 1989-1996, and an average increase of only 4% from 1997-2004. In addition, HYSPLIT back-trajectory model was used to determine that when ambient air arrived from the high ammonia emissions source region, ammonium concentrations in precipitation were enhanced. For the Southeast United States domain, analysis shows that NH_4^+ concentrations at various sites generally increased with increasing NH_3 emissions from within the same region. Similar analysis has been performed over the Midwest United States and the similarities and differences are discussed.

Introduction

Agricultural-related ammonia (NH_3) emissions from crops and animals provide a means for the formation of ammonium ion (NH_4^+) in the atmosphere, through the neutralization of acidic compounds. These two compounds, NH_x (= NH_3 + NH_4^+) are beneficial to plant growth and act as nutrients at relatively low concentrations, but can cause severe acidification problems, leading to eutrophication of water and decline in forests. Because of this, there is great need to study the effects of the ammonia emissions from agricultural, including their concentration, distribution, and transport, so that a better understanding of effective means to control or reduce excess amounts of ammonia and ammonium deposition.

Numerous governmental regulations, locally, regionally, and nationally have been set in order to curb the negative effects of excess NH_x levels, and there also exists a need to quantitatively determine the effectiveness of these regulations and hypothesis ways to improve there usefulness. Combining data from several different sources, this study attempts to provide generalizations in the trends of ammonia emissions, ammonia concentrations in the atmosphere, and ammonium concentrations in wet deposition. Comparisons were made between NH_x characteristics in the Midwest United States and the Southeast United States, providing a policy framework to this analysis based on the ammonium in precipitation.

Methods

Data Selection

For the purpose of comparison between the Midwest and Southeast United States, 16 states were chosen as part of the study. The states of Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, and Tennessee were defined as states in the Southeast United States. The Midwest United States was defined as the states of Illinois, Indiana, Iowa, Michigan, Minnesota, Missouri, Ohio, and Wisconsin.

In order to estimate ammonia emissions, the 2002 Census of Agriculture data was used. County level data of the population of cattle (both beef and dairy), horses, hogs (both sows and fattening pigs), sheep, broilers, chickens (including laying hens, young pullets, and more mature pullets), and turkeys were obtained. In addition, the acres of fertilized land were also obtained. Finally, the results were compared with those of the Carnegie Mellon University Ammonia Model to test for validity (Carnegie).

For ammonium concentrations in the atmosphere associated with aerosols, data from 22 sites of the Clear Air Status and Trends Monitoring Network (CASTnet) was obtained. CASTnet is a network of rural sites that collect site-specific measurements of total deposition and is the source for dry acidic deposition. The sites measure weekly average ambient atmospheric concentrations of particulate NH_4^+, as collected on a Teflon filter. The sites chosen have continuous data measurements from 1989-2004, so data was readily available for a long-term study such as this

Next, data on NH_4^+ concentrations associated with precipitation were obtained from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). From the data set of over 200 sites, 59 were chosen (30 from the Midwest United States and 29 from the Southeast United States). These sites have collected data weekly since 1978, so again contained extensive data to be used for this study. In addition to using specific NAPD sites, the 2002 ammonium ion concentration in precipitation map was analyzed and compared to that of the calculated emissions.

The HYSPLIT (Hybrid Single-Particle LaGrangian Integrated Trajectory) model was used to determine whether or not atmospheric transport was playing a role in the periods of high NH_4^+ concentrations over sites in North Carolina. HYSPLIT is a joint effect between NOAA and Australia's Bureau of Meteorology. It is able to compute air parcel simulations and dispersion and deposition simulations. For this study, HYSPLIT was used to perform a "backwards" dispersion model run for specified time periods at each site. The model assumed puff dispersion, where the puff expands and splits into several new puff each containing a portion of the pollutant mass. The dispersion shows the source region where the pollutant concentrations are coming from, and is therefore beneficial in determining if the swine facilities played a role in the ammonium concentration for that time period. For each model run, a 48 hour 'backwards' dispersion of deposition was performed from a source height of 100m.

Data Analysis

The first goal of the study was to develop a spatial representation for agricultural ammonia emissions over both the Southeast United States and Midwest United States. To develop the emissions inventory, the data from the 2002 Census of Agriculture from the United States Department of Agriculture (USDA) was used. Since the data was county level, emissions were assumed to be constant throughout each individual county. To calculate the emissions total for each county, the animal population inventory numbers were multiple by an animal-specific emissions factor, in kilograms of ammonia per animal per year. These emissions factors have been obtained through experimentation and mass balance calculations, generally done in Europe, so there could be a some degree of error, since animal practices vary greatly between the two continents. In addition, the animal's specific diet can highly alter the NH_3 emissions. Other factors, such as temperature, humidity, and waste handling, add to the uncertainty of the exact value of the emission factors. The final emission factors chosen to be used in the study were the same as those in an Aneja, et. al. (2003) study in which similar analysis was perform on 1997 Census of Agriculture data. The emission factors used are shown in Table 1. The total emissions per county were used to develop a spatial distribution across the two regions as well as to compare and contrast various characteristics of the distribution.

CASTnet and NADP data was then used to develop statistical analyses of several locations to determine the correlations between NH_3 emission, NH_4^+ concentrations in ambient air, and NH4 concentrations in precipitation. In addition, sites in North Carolina were analyzed both before and after the installation of the hog moratorium to determine its effectiveness.

Results

A map of the annual county-scale agricultural ammonia emissions was developed.

As shown on the map in Figure 1, emissions values are highest over southeastern North Carolina, in the heart of an intensive swine industry region. Emissions levels in these counties exceeded 10,000 kilograms per square kilometers. Various counties along a belt stretching from north-central Alabama across northern Georgia and South Carolina and to into southeastern South Carolina had emissions levels well in excess of 5,000 kg/km^2. Maximum values over the Midwest were significantly lower, with highest values over several counties in western Ohio and central and western Iowa. Table 2 lists the top 10 county in terms of annual agricultural emissions for both the Southeast United States and Midwest United States. Again, it can be noted the excessive values over southeastern North Carolina caused by the hog population and over portions of northern Alabama and Georgia, caused mainly due to the explosive growth of the broiler industry in those regions. The top 10 counties in the Midwest are characterized by significant beef cow populations across northwest Iowa, large poultry farms in Ohio, and hogs across Iowa and Indiana. The relatively low extreme values in the Midwest can be explained by the fact that livestock in the Midwest is more commonly larger, such as hogs and cows, which take up more space and are more difficult to densely populate, whereas the Southeast's livestock inventory has a much higher percentage of smaller animals, namely broilers, which can easily be immobilized into densely populated facilities.

Table 1. Emission Factors used (source: Aneja et. al. 2003)

Source	**Emissions Factor**
	(kg NH_3 animal-1)
Beef Cattle	10.2
Dairy Cattle	28.04
Horses	8
Hogs and Pigs	
Sows	16.43
Fattening Pigs	6.39
Sheep	1.34
Broilers	0.28
Chicken	
Laying Hens	0.37
Pullets 13-20 weeks old	0.269
Pullets <13 weeks old	0.17
Turkeys	0.858

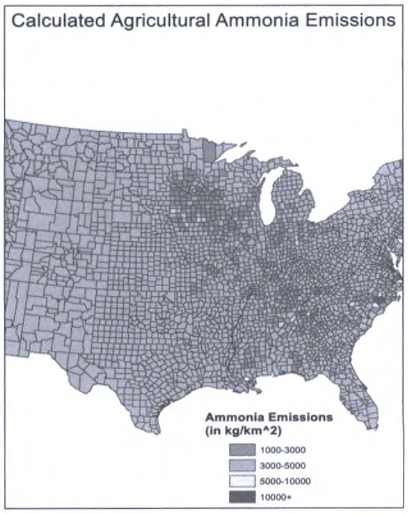
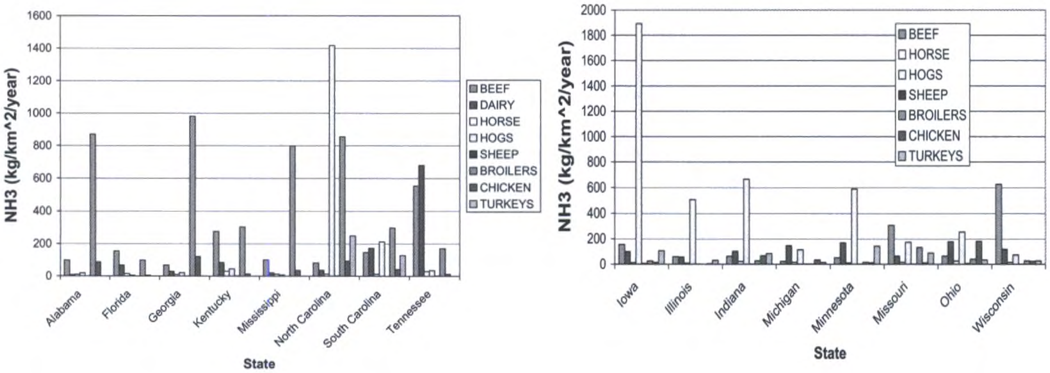


Figure 1. Spatial distribution of NH_3 emissions (kg/sq. mile/ year).

Perhaps the most obvious distinction between the two regions in terms of agricultural ammonia emissions is the source of the emissions. Great variation in terms of the major type of livestock produced exists between the two regions. Figure 2a and 2b shows the average NH_3 emissions deriving from specific agricultural sources in the Southeast and Midwest, respectively.The figures indicate the high totals over the Southeast United States in general come from broilers, but with the distinct exceptions of North Carolina in terms of hog emission as well as the dairy and beef cow industries in Tennessee. In contrast, the Midwest United States has its high totals deriving mainly from the hog industry, especially over Indiana, Iowa, and Minnesota. Cows, in particular beef, play a major role in agricultural ammonia emissions over Wisconsin and Missouri.

Table 2. Ten Counties with Highest Annual Agricultural Emissions

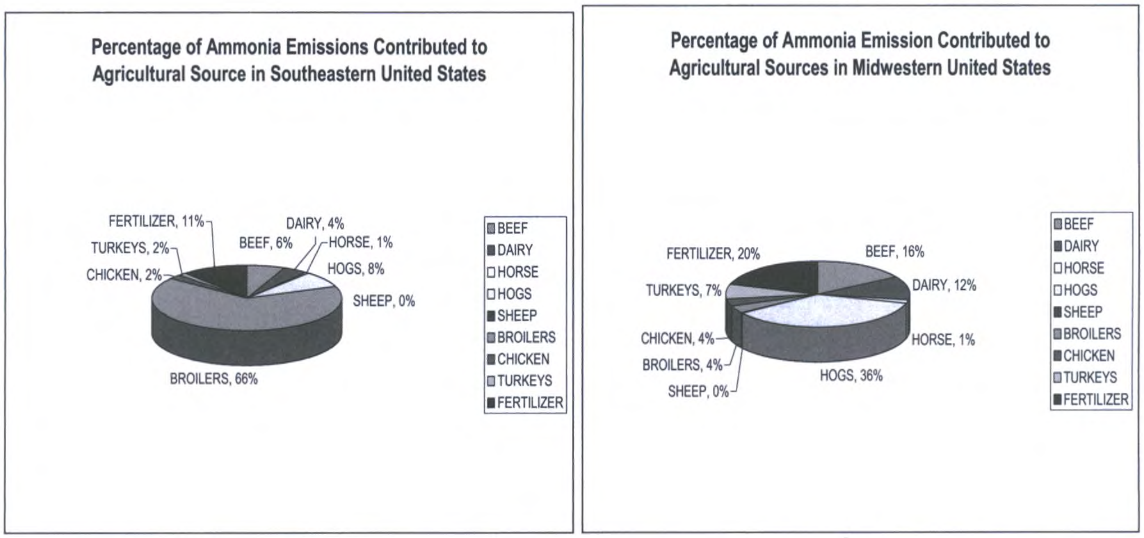
SOUTHEAST	**NH_3 (kg/sq. mile/yr)**	**MIDWEST**	**NH_3 (kg/sq. mile/yr)**
Duplin County, NC	24209.41	Mercer County, OH	12943.77
Sampson County, NC	19569.96	Hardin County, IA	10689.74
Franklin County, GA	14858.32	Hamilton County, IA	10592.47
Greene County, NC	13687.89	Sioux County, IA	9511.132
Wayne County, NC	12711.48	Darke County, OH	8606.599
Madison County, GA	10662.38	Buena Vista County, IA	7701.534
Kullman County, AL	10227.02	Martin County, MN	6918.426
Habershan County, GA	10132.06	Washington County, IA	6852.765
Banks County, GA	9813.943	Carroll County, IA	6797.724
Union County, NC	9776.172	Dubois County, IN	6268.582



(a) **(b)**

Figure 2. Total ammonia emissions from specific agricultural sources, by state, in the Southeast (a) and Midwest (b) United States.

In terms of the regions as a whole, the Midwest had roughly two-fifths of its total agricultural emissions stemming from hogs, with 16% and 12%, respectively, coming from beef and dairy cows. Fertilizer attributed for 20% of the emissions, whereas turkeys, chickens, and broilers combined to contribute 15%. In the Southeast, an overwhelming 43% of agricultural emissions of NH_3 came from broilers, with 11% deriving from fertilizer, and 16% stemming from the hog industry. Beef and dairy cows made up 12% and 9% respectively, and chickens and turkeys contributed 4% each. A previous study from five years early over the same Southeast region reported 33% broiler contribution, 28% beef cattle, 12% hog and 12% fertilizer (Aneja, 2000).This indicates that the broiler industry is rapidly growing, while the beef industry is declining over the region. The details of the relative contribution of each specific source to the total emissions for the region are shown in Figure 3.



a b

Figure 3. Emissions from specific agricultural sources, by region [Southeast (a) and Midwest (b) United States]

In comparing spatial distributions of agricultural ammonia emissions between the two regions, the Southeast has a much greater deviation in emissions locally. One of several explanations of this is that the Southeast United States is characterized by a more complex terrain, which mountains, swamps, and forests all separating localized areas of intensive agriculture. In addition, the great and more urbanized population of the Southeast again provides a more localized nature to agricultural areas. The Midwest, in contrast, is characterized by flat or gently rolling open plains, and with a much less dense population, there is a great uniformity to the intensity of agriculture in the region, allowing for more extensive, yet relatively moderate levels of agricultural ammonia emissions. Another possible explanation is the aforementioned fact thatlivestock in the Midwest is characterized by larger animals (which make up about 64% of the emissions, as opposed to 37% in the Southeast), which cannot be as densely populated as the smaller animals of the Southeast. Figure 4 shows the average standard deviation between emission totals in counties of the states included in the study. It is clear the variation in emissions is much greater in the Southeast than in the Midwest, which the highest variation in the states with the highest overall emissions totals as well as those with the highest percentages of small animal inventories.

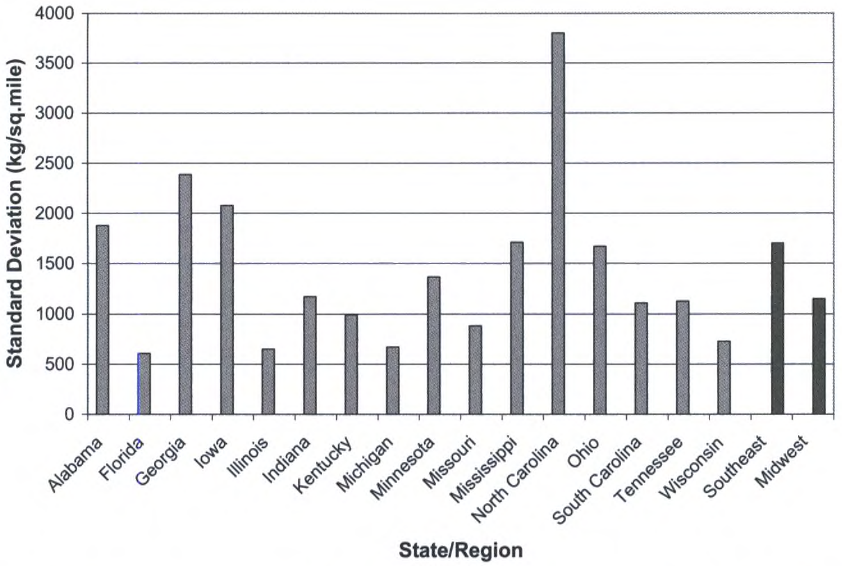


Figure 4. Standard deviation of ammonia emissions between counties in specific states.

In comparison with the model, the results were similar. The Carnegie Mellon emissions model produced slightly lower emissions totals overall, especially over the Southeastern United States.

Conclusions

Calculating ammonia emissions totals using animal inventories and emission factors can provide a useful means of depicting the spatial scale, distribution, and characteristics of agricultural related ammonia emissions at the county level. Improvements are needed in the accuracy of the emission factors on animals in the United States as well as diet specific emission factors, which will greatly enhance the plausibility of these estimates. The estimates provide a means of correlation ammonia emissions to ammonium ion concentrations, both in ambient air and in precipitation. A reasonable positive correlation seems to exist, but future work is needed to add in other factors which may affect the transport, deposition, and chemical transformation of both ammonia and ammonium ion, particular with regards to meteorological parameters and non-agricultural related emissions.

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

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Abstract

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

Characterization of Volatile Organic Compounds and Odors by *In Vivo* Sampling of Beef Cattle Rumen Gas Using Solid Phase Microextraction and Gas Chromatography-Mass Spectrometry-Olfactometry: Implications for Gaseous Emissions from Livestock

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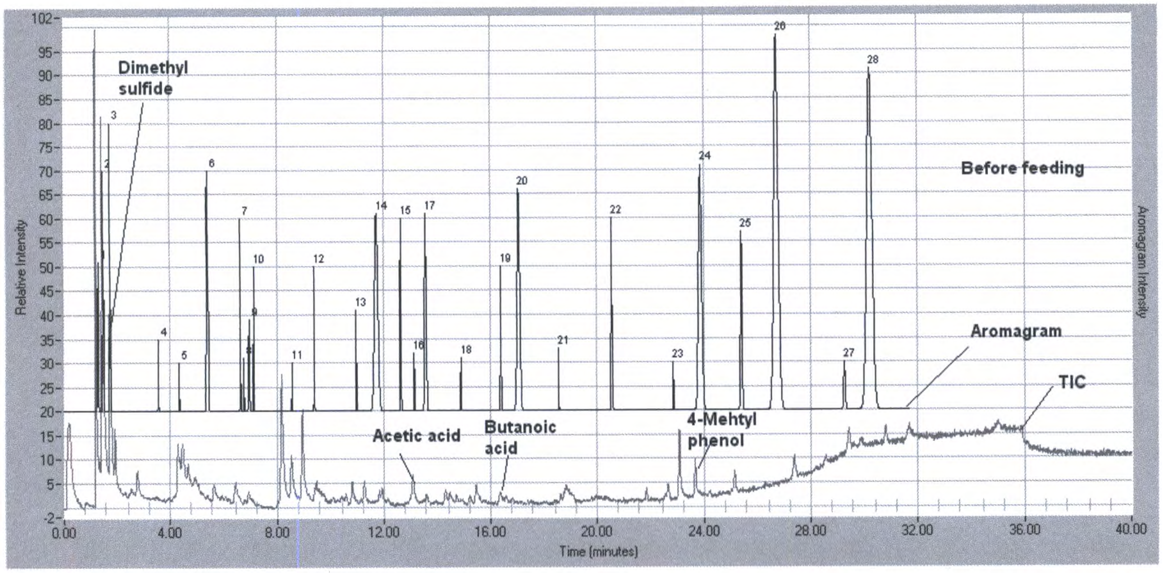
Abstract

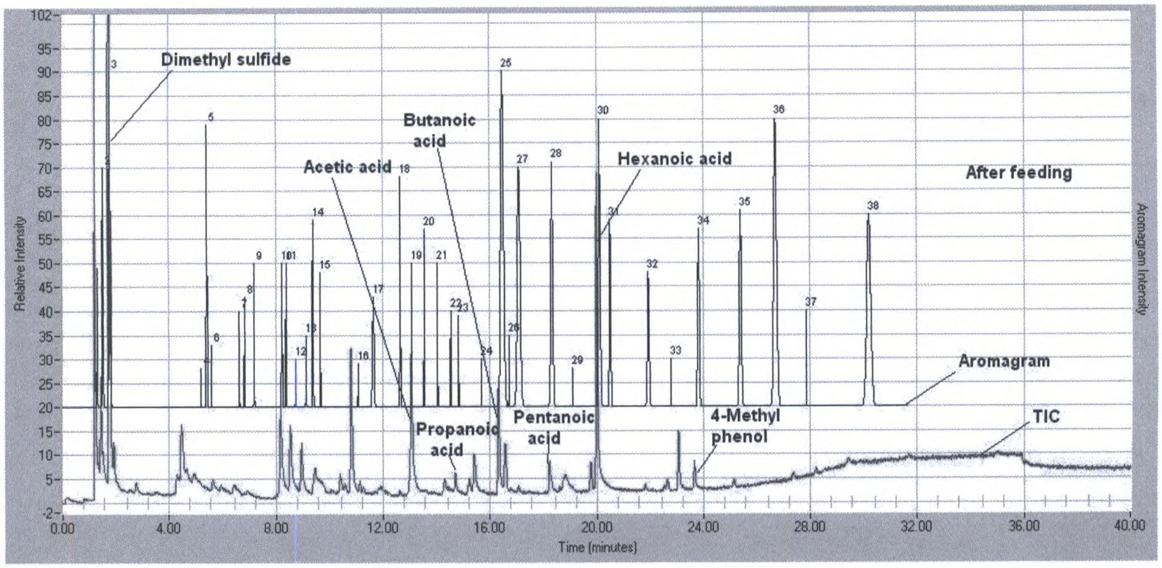
Cattle production is associated with aerial emissions of odor, volatile organic compounds (VOCs) and other gases originating mainly from manure and the animal itself. Chemical composition of rumen liquid and gas can affect aerial emissions. Rumen headspace is saturated with compounds produced during digestion. Many studies have focused on the characterization of ruminal fluid to determine the nature of microbial fermentation. However, little is known about the composition of rumen gas and its implication for gaseous emissions. This study was conducted to investigate the feasibility of *in vivo* sampling of rumen gases. A novel device allowing for headspace solid phase microextraction (SPME) sampling through the cannula was designed, refined, and used to collect rumen gas samples from three steers for three days. Rumen gas samples were extracted with 85 µm PDMS fibers using 1 to 10 min sampling times. Samples were analyzed using GC-MS-Olfactometry system allowing for simultaneous VOCs/odor evaluation.

This study identified 50 VOCs belonging to 10 chemical function groups and confirmed 31 of them with standards. The identified VOCs had a wide range of molecular weight (MW) (34 to 184), boiling point (b.p.) (-63.3 to 292 °C), vapor pressure (v.p.) (1.4E-03 to 1.56E+04 mm Hg) and water solubility (0.66 to 1E+06 mg/L). Odorous gases included those also emitted by manure such as VFAs, phenolics, indolics, sulfides and thiols. Twenty two compounds have an odor detection threshold (ODT) of less than 1 ppm. Four compounds are classified as hazardous air pollutants. Approximately 54% of the compounds have an estimated atmospheric lifetime of < 24 hr. Twenty seven odorous gases were then selected for further comparisons concerning the effects of feeding, steers, and sampling days.

The amounts of VFAs, sulfide compounds, phenol, and skatole of rumen gas after feeding were higher than those before feeding though a larger sample group must be studied to determine variation among compounds and animals. The total odor of rumen gas after feeding was also stronger than that before feeding (Figure 1). Similarly, the odor intensity of VFAs, sulfides, skatole after feeding rumen gas was higher than that before feeding. These results indicate that rumen gases can be an important source of aerial emissions and odor. Solid phase microextraction-GC-MS-O can be a useful tool to elucidate feed digestion and its relation to odor and VOC formation in cattle.



Part A



Part B

Figure 1. Comparison of total ion chromatogram (TIC) (lower, red line) and aromagram (upper, black line) of rumen gas between before feeding (Part A) and after feeding (Part B). Samples were collected using Carboxen/PDMS 85 µm SPME fiber and 5 min *in vivo* rumen sampling time. Samples were analyzed on a multidimensional GC-MS-Olfactometry system. Numbers signify odor/aroma events.

Synthetic CAFO Odor Formulation; an Effective Technique for Validation of Odorant Prioritizations

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Abstract

Establishing that a consensus subset of priority odorants is definable for CAFO operations is essential if sensory 'only' based monitoring protocols are to be successfully translated to objective alternatives which are instrument 'primarily' with sensory oversight based. This paper presents the results of recent efforts by the authors to use synthetic CAFO odor matching formulation development as a tool to help validate recently reported GC-Olfactometry based odorant prioritizations. Synthetic odor matching is a technique which has been used successfully by these authors in past consumer malodor / malflavor complaint investigations to support proposed odorant impact prioritization conclusions. In this case, an attempt is made to match swine CAFO downwind odor using the minimum number of odorants from the much larger 'potential' odorant field. Preliminary results are presented relative to development and evaluation of a first pass, minimum subset 'swine farm downwind' odor match formulation. The target test blends have been developed in an effort to demonstrate the proposed prioritizations as well as demonstrate the important concepts of 'character defining' odor impact and the 'context' dependent nature of perceived odor acceptability. Defining CAFO odor to the fewest number of key odorants has important implications for odor monitoring, control and remediation strategies.

Key words: malodor analysis, agricultural odor analysis, farm odor, GC-Olfactometry, GC-O, solid phase microextraction, SPME, multidimensional gas chromatography, livestock housing

Introduction

During the past two decades, hundreds of potential odorants have been reported in the literature for CAFO odor sources (Schiffman at al. 2001; Oehrl et al. 2001; Willers et al., 2003; Mosier et al., 1973; McGinn et al., 2003; Keener et al., 2002; Hutchison et al., 1982). However, recent work by these authors (Wright et al., 2005; Cai et al., 2006; Koziel et al., 2006) as well as others suggests that from this very large suite of potential odor contributors, community odor complaints (i.e. at distance downwind from the CAFO sources) may be largely driven by a relatively small subset of odorants drawn from this very large field. The concept of such prioritization relative to downwind odor impact, however, has not been without controversy within the industry. This controversy appears to have ranged from complete denial that any such prioritization of key odorants is definable for this application to simple differences with regard to the minimum critical odorant field size, composition, potential synergistic effects among key contributors or simply the impact priority ranking of the odorants within that subset. As an example of the latter, synthetic CAFO odor matching formulations reflecting variations in size and odorant composition of the odorant field have been previously reported. (Zahn et al. 2001) reported good odor match results with a formulation consisting of 20 prioritized odorants. (Qu et al. 2004) reported on good odor match results with a formulation consisting of 16 prioritized odorants. Clearly, the number of odorants reflected in these proposed formulations represent a considerable reduction in numbers relative to the total field of up to 440 discrete 'potential' odorant emissions from swine CAFO sources (Schiffman et al. 2001). These formulations clearly represent reduced number prioritizations relative to the total potential odorant field. However, Multidimensional Gas Chromatography –Mass Spectrometry-Olfactometry (i.e. MDGC-MS-O) odor profile development work by these authors (Wright et al. 2005) suggests that the size, composition and priority rankings of these minimal subset formulations can likely be further reduced to an even smaller odor 'marker' subset without significantly sacrificing odor match closeness. Such odorant field size reduction is important for the simplification of the challenges presented by instrument based sampling, transportation, storage and analysis. For example, it is obvious that these challenges are greatly reduced if the target field is reduced from the previously reported 440 potential odorant field to a three to five component prioritized 'marker' odorant subset.

Based upon previously reported MDGC-MS-O odorant prioritization ranking profiles relative to swine CAFO emissions a series of exploratory odor matching formulations were prepared consisting of five prioritized odorants; p-cresol, butyric acid, isovaleric acid, 2-amino acetophenone and 4-ethyl phenol. A master blend was prepared which attempted to match the approximate component headspace concentration ratio profiles developed during past equivalent collections carried out downwind but near a representative swine barn source in Iowa. An attempt was made to develop a formulation and delivery system which would ensure ease of preparation and speed of presentation during the relatively extensive odor match survey interviews which were ultimately planned to evaluate the closeness and recognizability of the synthetic to natural odor match. The actual odor match survey work is believed to be essential for the development of a reasonable level of odorant prioritization consensus. The formulation and survey interview protocol were developed with the intention of targeting a range of panelists from both within the industry and from the communities proximally located downwind of representative sources. The results reported herein relate to the development of the first pass, minimal subset formulation and associated survey protocol. The results of the actual formal survey interview work will be reported at a future meeting.

Materials and Methods

Multidimensional Gas Chromatography-Olfactometry-Mass Spectrometry:

MDGC-O-MS is an integrated approach combining olfactometry and multdimensional GC separation techniques with conventional GCMS instrumentation. A commercial integrated AromaTrax™ system from Microanalytics (a MOCON Company) of Round Rock, Texas was used for the GC-olfactometry profiling work in support of the work presented below. Details regarding hardware and operational parameters have been described in detail in past publications (Wright et al., 2005; Cai et al. 2006) and will not be restated here.

Sampling:

Solid Phase Microextraction (i.e. SPME) (Chai and Pawliszyn, 1998, Chai and Tang, 1998; Cai et al., 2006) utilizing a 1 cm Carboxen modified PDMS - 85 μm fiber was the headspace sampling technique which was utilized for the required odorant headspace profiling determinations and associated synthetic headspace concentration ratio matching requirements. Reference target environment SPME collections were carried out by direct fiber exposure of the representative swine barn environment – utilizing variations in downwind distance for cross-comparison purposes. All SPME collections were carried out under ambient conditions.

Synthetic Odor Match Formulation:

Prioritized Odorants: p-cresol, butyric acid, isovaleric acid, 4-ethyl phenol and 2-aminoacetophenone

Approximate Profile Response Ratio (MS-SIM responses for 4 of 5): 25 : 19 : 3 : 1

(2-aminoacetophenone below detection limit – optimized from delivery solution by iterative sensory assessment).

Odorant Delivery Solution: Food grade (i.e. low odor) monopropylene glycol

Odorant Delivery Concentrations (Near source): p-cresol = 110 ppm; butyric acid = 355 ppm; isovaleric acid = 90 ppm; 4-ethyl phenol = 28 ppm; 2-aninoacetophenone = 0.17 ppm (individual solutions)

Synthetic Odorant Delivery Procedure:

Odorant Delivery Mechanism: From filter paper substrate (1/4 disc leaf from double halving 150 mm diameter Whatman # 4 filter paper). One drop of the target odorant solution applied ~ 1 cm back from the curved leading edge while in a flat, horizontal orientation. After disappearance of the solution gleam into the paper the origin point of the leaf is grasped by the panelist for assessment. The odorant emission is presented in a rapid fan motion as the leading edge of the fan leaf is brought increasingly closer to the nose of the panelist. Multiple fan leaves can be grasped together and fanned simultaneously in order to simulate the composite odor effect of multiple individual odorant applications. A simple paper clamp device can be used to secure, align and separate the individual leaves during a multi-leaf / multi-odorant assessment.

Synthetic Odor Match Development and Survey Results:

Developmental odor match evaluation results: Four of six research collaborators charged with evaluation of the swine barn odor match formulations were in agreement with the following statements regarding the final blend as outlined above.

- The blend does carry a distinct, recognizable 'barnyard' / 'swine barn' downwind odor character.
- Selective removal of the p-cresol leaf from the multi-leaf / multi-odorant assembly significantly reduces the distinct, recognizable 'barnyard' / 'swine barn' downwind character.
- The p-cresol leaf alone, without modification from the four other prioritized odorants appears to still carry much of the recognizable characteristic odor.

As of the time of this writing the remaining two research collaborators had not reported their assessments and therefore, for purpose of this report, are assumed to be in disagreement with the above odor match assessment statements. Combined final results will be presented at a later date.

Survey odor match evaluation results: The actual field survey portion of this study has not been completed as of the time of this writing. Efforts are proceeding to get the appropriate Institutional Review Board approvals in place in advance of going forward with the actual field survey phase of the project. The combined results will be presented at a later date.

Results and Discussion

Experience has shown that a common characteristic of natural materials and processes is that they typically emit a complex mixture of volatiles representing a wide range of odor potency and headspace concentration. Although this complex suite of odorants does combine to form the composite odor character of the source it is atypical that all (or many) of those 'potential' odorants share equal impact significance relative to the generally recognizable composite odor character. In practice, it is in fact, more typical that a smaller subset of high impact odorants can be defined for the source (Belitz et al. 1999) which, when synthetically combined to emit in appropriate proportions, can represent a reasonable synthetic odor 'match' to the natural source. In many cases what begins as a very complex suite of potential odorants can be reduced to a generally recognizable synthetic match utilizing a small subset of high impact, 'character defining' odorants from the much larger emission field. Simply stated, if upon composite odor assessment of a material or environment, the odor character of an individual odorant is easily discernable from the complex odorant matrix which accompanies it, that individual odorant has to be considered of greater importance relative to overall odor impact. As an example, in spite of a relatively complex odorant emission profile the characteristic aroma of beets is heavily defined by geosmin, a single, extremely potent, 'character defining' odorant (Belitz et al. 1999) . In fact, many individuals familiar with the composite aroma of beets, when presented with a synthetic blend containing only geosmin, will recognize the aroma and make the association with natural beets. Therefore, from the original field of scores of 'potential' odorants emitted by natural beets, geosmin clearly represents,a definable high priority emission relative to beet aroma. The past and current work by the authors represents an attempt to determine if such a high impact subset of prioritized odorants is definable for a much different odorous source, swine CAFO operations.

MDGC-MS-O techniques have proven to be very effective in enabling the development of odorant priority ranking profiles relative to even extremely complex natural and synthetic odor sources (Wright et al, 1997, Nielsen et al., 2004, Nielsen et al. 2001a; Nielsen et al 2001b). However, a different challenge is presented relative to the validation of such prioritization rankings through consensus development within a wider target audience. Obvious target audiences with respect to the swine CAFO odor issue are citizenry within the downwind communities, CAFO operation owners and managers, governmental regulators and CAFO researchers. Although the MDGC-MS-O techniques are effective in enabling the development and refinement of the odorant prioritizations relative to a limited number of individuals within the latter group it is much too complex a technology to attempt to utilize directly to explore for a wider consensus within the larger target population groups. An effective alternate strategy is to take the odorant priority ranking profiles which has been developed by MDGC-MS-O and use the results to develop a simplified survey protocol based upon minimal synthetic odor match formulations (i.e. as in the geosmin to beet aroma match). Such an approach enables a proposed odorant priority based formulation to be quickly and relatively simply surveyed by a statistically appropriate number of individuals within the key target audiences. With respect to the issue of CAFO downwind odor complaints it is obvious that the target audience of highest priority will be citizenry within the affected downwind communities.

Based upon the author's previously reported MDGC-MS-O based odorant prioritization results (Wright et al. 2005; Koziel et al., 2006) initial synthetic odor match formulations targeted a minimal subset of high impact odorants. Specifically, five odorants were selected from among the hundreds of 'potential' odorants which have been identified as emmisions from swine CAFOs (Schiffman et al., 2001); p-cresol, isovaleric acid, butyric acid, 2-aminoacetophenone and 4-ethyl phenol. Optimization of the initial blend involved an iterative process which attempted to balance the component emission characteristics relative to the propylene glycol solvent with targeted headspace concentration ratio values as previously determined downwind from a typical swine CAFO operation (Koziel et al., 2006). Instrument MS-SIM response ratio values were utilized to optimize the initial relative odorant headspace concentrations with respect to four of the five components; p-cresol, butyric acid, isovaleric acid and 4-ethyl phenol. However, the optimization of the fifth component, 2-aminoacetophenone, was attempted through sensory assessment only due to the fact that MS responses for this extremely potent odorant were below its detection limit under the referenced downwind site sampling conditions. The primary synthetic odor match formulation targeted a sample point downwind but relatively near the source swine CAFO. Although this point was selected as the distance for initial match focus, it is possible that a simple dilution process relative to the odorant source solution can be used to develop 'first pass approximation' solutions reflecting the natural dilution effects which are brought about by increasing downwind distance. Although this possibility exists due to the Henry's Law and the linear relationship between volatile solutes in dilute solutions the relationship has not been confirmed experimentally for this solvent / solute system.

In addition to developing an optimized 'from solution' odorant delivery matrix for the prioritized odorant suite it was also necessary to develop a simple and reproducible mechanism for presenting the composite odorant to the survey panelists. As described in the previous section the authors settled on a multi-leaf, multi-odorant, filter paper substrate format. The multi-leaf format enabled rapid assessments to be made regarding relative impact of individual odorants through inclusion or exclusion from the combined multi-leaf composite. Separation of the individual target odorant solutions enabled the aforementioned odor impact isolation as well as minimized the likelihood of target odorant loss through interaction with other odorants. Odorant delivery from a single drop glycol application to the paper substrate appeared to yield a relatively stable long term (i.e. 20 to 45 minutes) composite odorant release with respect to the initial target odorant formulation. In addition the individual odorants exhibited good long term stability with room temperature storage over several weeks duration.

The odor match survey protocol which was adopted for this study is a multi step probe of odorant recognition responses from the target audience participants. This stepwise process was structured as follows:

- **Memory only** – Memory only 'best match' blind assessment made without any suggestion or cues presented to the participants. This represents a test of the participants ability to differentiate a series of diverse odors and associate these with common materials from memory.
- **Memory with written reminder cues -** Memory with reminder cue 'best match' format. The participant is asked to select from a written list of 10 to 15 possible sources, the best source match for each of the 3-4 unknown odorants or odor blends which they are being asked to evaluate. This process represents a test of the participant's recognition ability when presented with an associated 'memory jog'. This step is important because it is often the case that individuals will know that they recognize an odor as being very familiar but can't make the association with the correct source when relying on memory alone. However, once presented with the associated source material or even a verbal 'reminder' the correctness of the association is often obvious (often frustratingly so).
- **Physical match -** Physical 'best match' format. This represents a test of the participants ability to physically match a series of diverse odorants and associate these with matching source materials

with which they are presented. The participants are presented with samples of common source materials and asked to perform a physical odor assessment and develop their 'best match' (i.e. canned beets and geosmin) to the unknown odorant probes.

- **Modified swine downwind with written reminder cues -** Memory with reminder cue 'best match' format. The participant is asked to select from a written list of 10 to 15 possible sources, the best source match for the original 5 component swine barn formulation which has been modified by the removal of the leaf which carries the p-cresol component. This process is effective for the determination of the level of impact of p-cresol alone relative to the balance of the field.

A separate questionnaire sheet is presented to the survey participant at each of the above stages of the survey. The stepwise format of the survey is designed to yield a graded impact significance. For example, a correct source match at the first stage (i.e. memory only) is the most significant match but may only be achieved by those individuals with frequent or long term familiarity with a target source (i.e. downwind citizenry, beet eaters etc). In contrast, a correct source match at the second stage (i.e. memory with reminder cues) is a less significant match but still must be considered significant relative to individuals with infrequent or minimal exposure to a target source (i.e. occasional visitors to downwind communities, etc). Lastly, a correct source match at the third stage (i.e. physical match) is a less significant match still relative to the previous two stages but must be considered significant relative to individuals with no previous exposure to a target source.

As outlined in the previous section, assessment results relative to the first pass odor match formulation are encouraging. Even though the odor match assessment data is very limited up to this point, it is believed to be significant that @ 67 % of the research collaborators agree that 1) the formulation carries a recognizable characteristic 'barnyard' odor 2) selective elimination of p-cresol alone significantly reduces this characteristic odor relative to the balance of the field and 3) the p-cresol leaf alone, separate from the influence of the remaining field, still appears to carry much of the target characteristic odor. These results appear to yield, at least, a first stage indication of a relatively high individual odor impact of p-cresol relative to CAFO downwind environments. It is possible that this impact may approach 'character defining' status under some operation and environmental conditions but this can only be established through the much broader 'target audience' survey work.

Conclusions

These odor match formulation development results appear to yield, at least, first stage confirmation of a high individual odor impact of p-cresol relative to the CAFO downwind application in general and the high density swine barn CAFO application specifically. They also appear to indicate that a relatively small subset of odorants (i.e. including p-cresol) from the complex volatiles emissions from these sources may account for the bulk of the negative impact relative to communities downwind of these sources. The perceived relatively high individual odor impact of p-cresol is particularly significant since its impact appears to approach 'character defining' status under some operation and environmental conditions. However, this increased status can only be confirmed through the much broader 'target audience' survey work. Particular attention appears to be warranted for p-cresol and other high priority semi-volatile odorants due to their apparent odor impact prominence and their well documented propensity for adsorption driven loss to the walls of plastic sample containers.

Acknowledgements

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Field Monitoring at California Dairies to Model ROG and Ammonia Emissions

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Abstract

A preliminary study of ROG and ammonia emissions from two dairies in the Central Valley of California used upwind/downwind canister sampling and a Gaussian plume model to predict emissions from general areas within the dairy operation such as the animal housing and the manure lagoon system. The estimated emmission rates were correlated with those predicted by other researchers using more complex methods (flux chambers) at the same locations. Monitoring and modeling conditions were such that five data sets and modeled emission rates were successfully completed in 2004. Two of those were correlated with flux chamber data from the same dairy. There are approximately 2500 dairies in California with a variety of management practices that may influence emissions. Currently the state and local air quality agencies are implementing air quality permits that may require adoption of control practices. There is very little research upon which to base the effectivness of these proposed control practices so a second phase of this project has been funded by the California State Air Resources Board. This second phase will expand the monitoring program to include additional components of ROG and a more intensive study of N compounds. An additional four dairies will be added to the original two. The additional sites will be selected to expand the range of manure handling practices in the study. Data and emission rates from the preliminary project along with results from the initial sampling will be available by spring of 2006. The monitoring program and the sampling systems developed for the second phase of the study will be detailed along with the initial data.

Modeling Study of Dry Deposition of Ammonia in North Carolina

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Abstract

Dry deposition is an important pathway contributing to the removal of ammonia from the atmosphere. A significant amount of NH_3 (~250 tons annually) is emitted in North Carolina owing to intensive animal and agricultural farming. A convenient way to parameterize the deposition flux specific to the surface/gas conditions is by estimating its deposition velocity. Studies have been conducted recently at rural agricultural sites in Europe and the United States to estimate the dry deposition velocity of ammonia over forests and farmlands. The average velocity reported in these studies was generally less than 5 cm/s. The objectives of the current study are to compare the simulated dry deposition amounts of NH_3 with measurements for two 1-month episodes during August and December, 2002 and to study the uncertainties associated with the dry deposition treatment of NH_3 in MM5/CMAQ. The models used are the PSU/NCAR mesoscale model (MM5) and the U.S. EPA Models-3 Community Multi-scale Air Quality (CMAQ) Modeling system. The observed values are obtained from the measurements conducted by Phillips et al. (2004). The dry deposition scheme used is the Models-3 M3DRY model. Statistics, time series plots, and spatial plots will be used to analyze the difference between model predictions and observed velocities. The effect of grid size will be contrasted by comparing the deposition velocity/flux results of 4-kms and 12-kms simulations over the domain. A sensitivity simulation with MM5/CMAQ will also be conducted after modifying the bulk surface resistance parameters, in particular, those used for the in-canopy resistance, to study the associated uncertainties to estimate the dry deposition velocity and flux. The results of the baseline and sensitivity simulations will be compared to suggest areas of improvement in the parameterization of the dry deposition of ammonia in the existing models. Disclaimer: Although this work has been reviewed by EPA and NOAA and approved for publication, it does not necessarily reflect their policies or views.

Condensed Tannin in Drinking Water of Cattle and Sheep to Reduce Their Urine Urea Excretion and Subsequent Ammonia Pollution

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Abstract

Methods are needed to reduce urine urea excretion and consequent ammonia emission that is associated with ruminant meat and milk production while not reducing productivity. Ingestion of small amounts of naturally-occurring condensed tannin by ruminants can reduce their urine urea excretion and improve their productivity. However, providing grazing ruminants with pasture forages such as birdsfoot trefoil (*Lotus corniculatus*) that contain condensed tannin is problematic. Therefore, I have conducted trials to determine if sheep and cattle will readily drink water containing small amounts of condensed tannin and found that they will. This paper reports results of a trial with a latin-square design where four wether sheep (mean body weight 64.8 kg ± 5.4 SD) were fed alfalfa (*Medicago sativa*) pellets (3.5% nitrogen) and given tap water or tap water with low (0.5% of daily dry matter intake (DDMI) assuming they drank similar amounts of this liquid as they did of tap water), medium (1.0% of DDMI with the same assumption) or high (1.5% of DDMI with the same assumption) amounts of quebracho tannin (QT) in it and their urine urea excretion was measured. There was a linear effect of QT intake on daily urine urea excretion as a percentage of nitrogen intake ($P = 0.03$). Ingestion of water containing the low, medium and high levels of QT resulted in reductions in daily urea excretion as a percentage of nitrogen intake of 3.5, 6.5, and 12.5%, respectively. Results from my other studies indicate that greater reductions in urine urea excretion may be possible by placing small amounts of condensed tannin in the drinking water of cattle and sheep. This can likely by done while maintaining or improving their productivity.

Introduction

Growing levels of nitrogenous compounds (e.g. ammonia, nitrates, nitrous oxide) in the environment are associated with human health and environmental concerns (Galloway et al., 1995; Vitousek et al., 1997; Burkart and James, 1999; Wolfe and Patz, 2002; Townsend et al., 2003). Urea in ruminant urine is an important precursor of these compounds (Doak 1952; Sherlock and Goh, 1984; Thomas et al., 1988; Misselbrook et al., 2000). Ingestion of forage containing condensed tannins by ruminants can improve their nitrogen use efficiency and reduce their urine urea concentration and overall nitrogen excretion (Egan and Ulyatt, 1980; Waghorn et al., 1987a and b; Waghorn et al., 1994), and the optimal daily intake of condensed tannin when ingested as a constituent of forage appears to be 2 to 4% of dry matter (DM) intake (Waghorn and Shelton, 1995; Min et al., 2003). For grazing cattle and sheep, the benefits described above are limited by lack of condensed tannins in most grasses and some important herbaceous forage species (e.g. alfalfa, *Medicago sativa*) and difficulty, for many areas, in establishing and (or) maintaining single or mixed species pastures with herbaceous forages that contain condensed tannins (e.g. birdsfoot trefoil (*Lotus corniculatus*) and sainfoin (*Onobrychis viciaefolia*)). For penned cattle and sheep, obtaining adequate intake of condensed tannins may be possible by mixing them with their feed, but obtaining appropriate and uniform intake of a feed supplement containing condensed tannins will be difficult when cattle and sheep are grazing (Bowman and Sowell, 1997). Therefore, the possibility of putting condensed tannin in the animals' drinking water to allow for consistent ingestion of low amounts of condensed tannin by grazing ruminants, improve their nitrogen use efficiency and reduce their urine urea excretion is worthy of evaluation especially considering that condensed tannins are often considered ingestion deterrents (Cooper and Owen-Smith, 1985; Villalba and Provenza, 2001). Intake trials with cattle and sheep at my laboratory have demonstrated that these ruminants will reliably drink normal amounts of water with low levels of condensed tannins in it, and the research herein reported demonstrates that their ingestion of small amounts of condensed tannin in water can reduce the amount of urea they excrete in their urine.

Methods

Four wether (castrated male) sheep (mean body weight 64.8 kg ± 5.4 SD) were kept in metabolism stalls in a barn maintained at 7.2°C. They were fed alfalfa (*Medicago sativa*) pellets (3.5% nitrogen, DM basis) at 2.5% of their body weight with half their ration fed at 0630 and the other half fed at 1530. Using a Latin-square experimental design each sheep was offered four different liquids (one per period) to drink in *ad libitum* amounts from a self-activated drinking bowl, and their daily intake of liquid was measured with a water meter placed on the supply line. The four liquids were tap water or tap water with low (0.5% of daily dry matter intake (DDMI) assuming they drank similar amounts of this liquid as they did of tap water), medium (1.0% of DDMI with the same assumption) or high (1.5% of DDMI with the same assumption) amounts of quebracho tannin from the quebracho tree (*Scinopsis balansae*) in Argentina. Quebracho tannin was obtained from the Tannin Corporation (Peabody, MA). For each of four periods, an 8-day adaptation phase preceded a 2-day collection phase in which daily urine output was measured and sampled using 12-hour collection intervals. Sulfuric acid was placed in the urine collection containers to prevent loss of urine urea. Urine samples were promptly frozen after collection and analyzed for urea concentration using standard veterinary diagnostic procedures. Mean urine urea output (grams/day) for both days of each period was determined as was forage nitrogen intake (grams/day) to produce the dependent variable daily urine urea excretion as a percentage of daily nitrogen intake. These data were analyzed using PROC Mixed (SAS 1996) with animal as the random variable. The covariance structure used was the variance components.

Results and Discussion

Mean liquid intakes for the 2-day collection phase for tap water, low, medium and high tannin solutions were 4.91, 4.56, 4.36, and 4.48 liters/day, respectively. Tannin intake that was necessary to achieve the desired intake of tannin and actual tannin intake for the low tannin liquid was 8.1 and 9.9 g/day, respectively. Tannin intake that was necessary to achieve the desired intake of tannin and actual tannin intake for the medium tannin liquid was 16.2 and 19.4 g/d, respectively. Tannin intake that was necessary to achieve the desired intake of tannin and actual tannin intake for the high tannin liquid was 24.3 and 29.2 g/day, respectively. Daily urine urea excreted as a percentage of daily nitrogen intake was 43.1, 41.6, 40.3, and 37.7% for the tap water and low, medium, and high tannin liquids, respectively. Daily fecal nitrogen output was 12.8, 14.0, 15.6, and 16.6 g/day for the tap water and low, medium, and high tannin liquids, respectively, but this nitrogen is not readily converted to ammonia as is urea in urine. Drinking the low, medium, and high tannin solutions resulted in urine urea outputs as a percentage of nitrogen intake that were 3.5, 6.5, and 12.5% lower, respectively, than that for tap water ($P < 0.0001$). There was a linear effect of quebracho tannin intake on daily urine urea excretion as a percentage of nitrogen intake ($P = 0.03$). These results are consistent with results of studies in New Zealand with sheep fed forages containing condensed tannins (Egan and Ulyatt, 1980; Waghorn et al., 1987a and b; Waghorn et al., 1994; Waghorn and Shelton, 1995; Aerts et al., 1999; Min et al., 2003). These results indicate that ammonia and nitrous oxide emissions derived from urea in urine spots produced by cattle and sheep grazing pastures of forage contain high levels of nitrogen may potentially be reduced by introducing small amounts of condensed tannin into the drinking water of these animals. Results from this study as well as work in New Zealand indicate that this procedure may also improve the nitrogen use efficiency of the ruminant livestock ingesting this liquid and potentially improve their productivity.

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Test Results of the use of a Wet Electrostatic Precipitator (wESP) for the Control of Gaseous Pollutants from Concentrated Animal Feeding Operations

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Abstract

Electrostatic precipitators (ESPs) have been in use in the industrial sector for the control of particulates for decades. Recent research has shown the potential capability of wet ESPs to control gaseous pollutants as well. Malodorous emissions from concentrated animal feeding operations (CAFOs) have raised serious concerns because of the potential risk these emissions pose to human health. Moreover these emissions cause nuisance in the surrounding neighborhood because of the persistent repulsive odor.

In this research, a wet ESP was tested to evaluate its performance in removing gaseous CAFO pollutants. Known concentrations of the gases responsible for the odorous emissions in the CAFOs were subjected to the corona discharge inside a wet ESP under varying experimental parameters such as energy input, gas flow rates and the residence time.

Preliminary results from experiments involving hydrogen sulfide, the main component responsible for odorous emissions in CAFOs have shown maximum removal efficiency of more than 70 % under wet ESP operations at low pressure drops and energy usage. The removal efficiency was seen to be the function of both the power supply and the residence time to a certain extent. The results of the experiments have also indicated that optimizing the experimental parameters can further increase the removal efficiency of the wet ESP.

Introduction

Obnoxious gaseous emissions from concentrated animal feeding operations (CAFOs) are of great concern from an environmental perspective as well as from a public health point of view. Moreover these emissions cause nuisance in the community because of the persistent repulsive smell [1]. Among others, gaseous pollutants such as hydrogen sulfide and ammonia are the major contributors responsible for the odorous emissions from CAFOs [2]. Studies have established a direct correlation between the health impacts among the workers in the animal farm houses and the emission levels of hazardous gaseous pollutants in such facilities, which indicates the gravity of the problem. This problem, therefore, needs immediate attention in order to find an appropriate remedial action [3].

This research was aimed to address this problem with the application of a control technology known as wet Electrostatic Precipitation (wESP). Wet ESPs have been in use in the industrial sector for decades specifically for the control of particulate pollutants. A literature review shows that wet ESP technology can be applied for the control of gaseous pollutants as well. Sabacchi et. al. reported up to a 99% destruction and removal efficiency for volatile organic compound (VOC) emissions applying a pulsed corona discharge in an ESP, with power consumption being competitive with the present technologies for VOC removal [4]. Yan et.al. have also showed that up to 75 to 80 % of SO_2 can be removed using the pulsed corona discharge with a reasonable power consumption [5].

Therefore in this project, a wESP has been tested to evaluate its performance in removing specific gaseous pollutants responsible for odorous emissions in CAFOs. The main objective of this research was to evaluate the use of wet ESPs and determine its potential technology for controlling CAFOs emissions.

Experimental Approach/ Methods

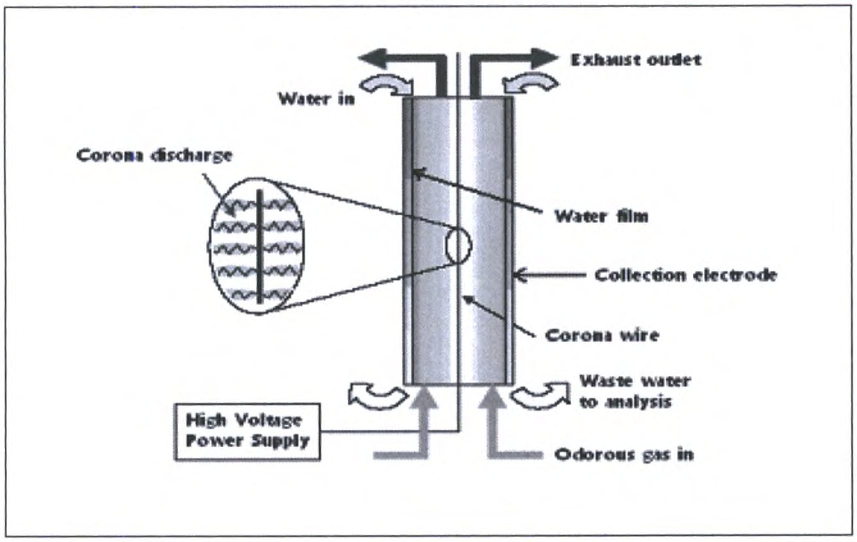

Figure 1

Wet ESP Design

As shown in the schematic in Figure 1, a 3 foot long, 0.25 inch thick and 7 inch internal diameter steel cylinder was used as the wet ESP. On the top inner portion of the cylinder a toroidal ring of copper with small perforations along its outer ring was attached along the ESP wall. The copper tube was connected to the water supply and the water was sprayed out through the perforations so as to maintain a film of water all along the inner surface of the ESP. A pump was used to recycle the water from the bottom to the top from where it was sprayed.

A threaded wire, 0.12 inch in diameter, connected to the power supply was adjusted in a vertical alignment at the central inner space of the ESP to act as the charging electrode. The ESP surface being grounded acted as the collection electrode. By adjusting the flow rate and the dilution ratio, a known concentration of gaseous pollutant, hydrogen sulfide in this case was allowed to flow through the cylindrical ESP from bottom to top, where it was subjected to the corona discharge created from the charging electrode.

Dilution of Hydrogen sulfide

One hundred precent pure hydrogen sulfide gas from a cylinder was injected into the dilution system where it was mixed with air drawn by a blower. The flow rate of the gas from the cylinder as well as the flow rate of the air drawn from the blower were adjusted so as to control the initial concentration of the pollutant gas to be fed into the wESP system. After achieving the required dilution ratio and therefore the required initial pollutant concentration, the flow of the diluted pollutant was allowed to pass to the bottom of the wESP. It was possible to adjust the gas residence time by means of bypassing a portion of the simulated CAFO air. Gas residence times from 2.1 to 6.0 seconds have been tested. The concentration of the gas was measured using a handheld 4 Gas Analyzer (Model TMX 415) so as to determine the inlet concentration. Likewise, the final flow rate through the ESP was measured using a standard pitot tube to determine the desired residence time of the gas in the ESP system.

As shown in Figure 2, a high voltage DC power supply was provided with the aid of voltage multiplier/transformer. The power supply discharges a capacitor (combination of charging electrode and collection electrode in this case) through a spark gap to generate a high voltage pulse. This configuration initiates the corona discharge along the corona wire which then extends out of the electrode thereby forming a corona zone surrounding the corona-wire itself. The collection electrode of the ESP as well as the voltage transformer was properly grounded so as to develop a very strong electric field between the charging and collection electrodes inside the wESP where the gas was subjected to the electric discharge.

Corona Generation

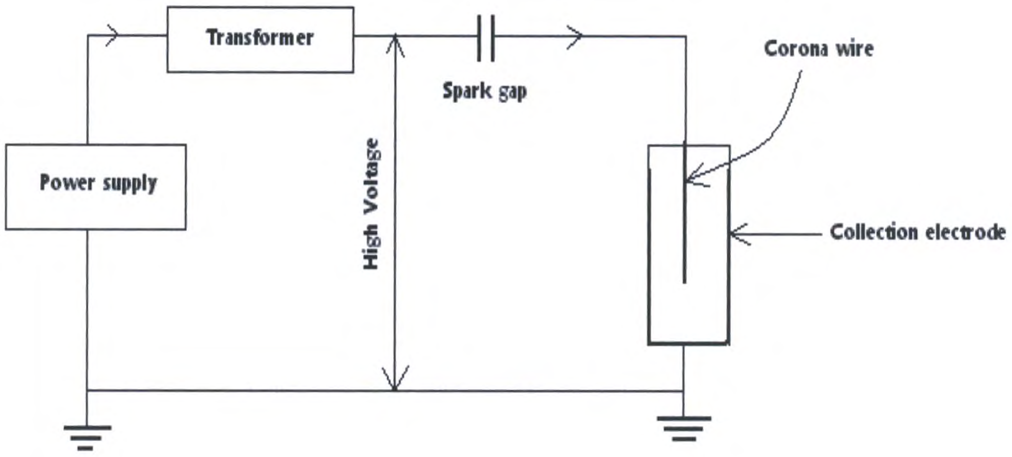

Figure 2

Charging Mechanism

Owing to the strong electric field, the gaseous pollutant is assumed to be charged in the corona region. There can be different possible pathways for the gaseous pollutants to get charged but different studies have indicated that electron attachment as the most likely dominant charging mechanism. Among other charging mechanisms, ionization seems not feasible because the energy requirement can be high for the formation of radicals owing to the presence of air and moisture along with the pollutant. Regardless of the mechanisms, the results indicate that the gaseous pollutant molecules are charged after being subjected to the strong electric field so that they migrate toward the grounded collection plates, where they interact in thin film of running water and are partially dissolved and washed out of the system.

In this regard, the main role of the corona discharge is assumed to minimize the gas phase mass transfer resistance as well as enhance the gas-liquid boundary layer mass transfer phenomenon by thinning the boundary layer due to the formation of the corona wind [6].

The treated gas comes out of the outlet where the final concentration of the gas is measured with the aid of an analyzer. Based on the initial and final concentrations of the gas, the removal efficiency of the wet ESP is determined in terms of percentage.

Results and Discussion

The results of the preliminary laboratory experiment have been tabulated and are given in Table 1 as shown below.

A single initial concentration of hydrogen sulfide (9 ppm) was subjected to three different corona strengths (power supply) ranging from 24.5 to 58 watts at four different residence times (approximately 2, 3, 4 and 6 seconds). The degradation of the pollutant gas during the wet ESP operation with respect to the residence time in three different power supplies can be visualized as in the graph shown below:

Int Conc. (ppm)	Res time (sec)	Corona strength	Power (watts)	Final Conc. (ppm)	Removal Efficiency (%)
9	2.1	35 kV, 0.7 mA	24.5	6.50	27.78
	2.9			6.00	33.33
	4.1			5.50	38.89
	6.0			5.35	40.56
	2.1	48 kV, 0.8 mA	38.4	5.00	44.44
	2.9			4.00	55.56
	4.1			3.50	61.11
	6.0			3.40	62.22
	2.1	58 kV, 1 mA	58	4.00	55.56
	2.9			3.00	66.67
	4.1			2.50	72.22
	6.0			2.40	73.33

Table 1: Experimental Results

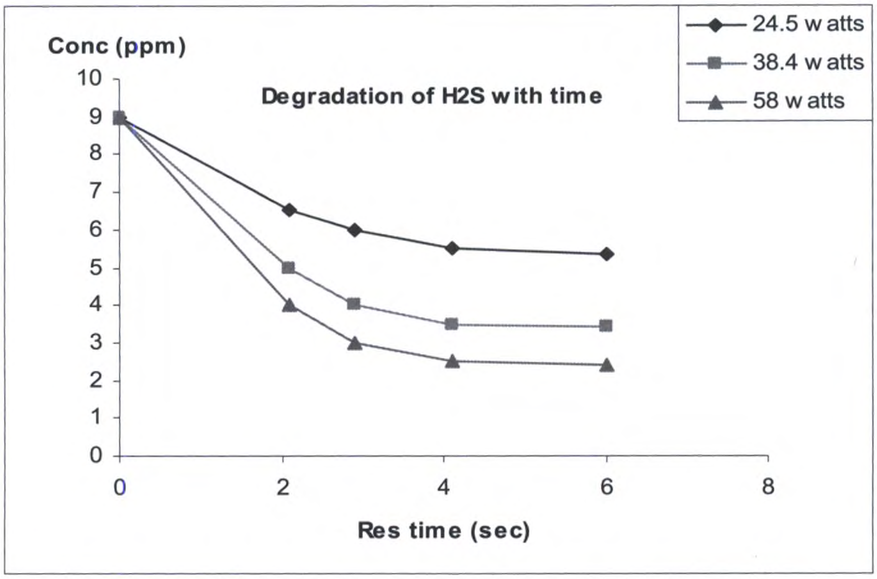

Figure 3

As obvious in the above graph, the degradation of the pollutant gas follows a sharp trend initially and the degradation rate diminishes as the residence time increases. The rate of degradation is seen to be maximum for the maximum power supply i. e. at 58 watts and minimum for the smallest power supply which is 24.5 watts.

The removal efficiency was measured on the basis of initial and final concentration of the gas and expressed in terms of percentage. The results showed that the removal efficiency ranged from almost 28 % to more than 73 % when residence time and power consumption were varied from 2.1 to 6.0 seconds and from 24.5 to 58 watts, respectively.

To analyze the effect of residence time as well as corona strengths, the above results obtained were graphed up as shown in Figure 3:

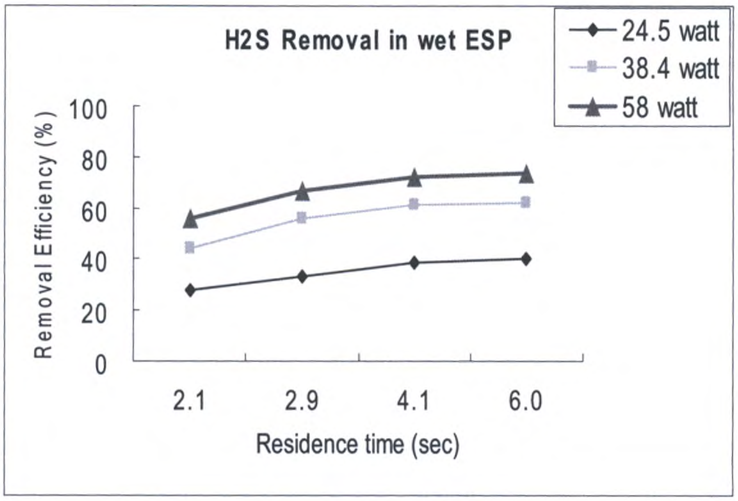

Figure 4

From Figure 3, the removal efficiency is found to increase with the increase in residence time, and with an increase in input power. This indicates that the removal efficiency is the function of both residence time and the input power supply. Sixty watts is the maximum power that can be supplied to the system and from Figure 3 it appears that applied power has a greater impact on removal efficiency than gas residence time. Our results indicate that he maximum removal efficiency that can be achieved for this system is ~ 70 % at 6-seconde residence time and 58 watts applied power.

Conclusion

The results from the preliminary experiment involving hydrogen sulfide have shown that wet ESP can be proved to be an effective technology for the control of obnoxious emissions from concentrated animal feeding operations.

Besides hydrogen sulfide, ammonia is another major source of odorous emissions in CAFOs but ammonia is highly water soluble as compared to hydrogen sulfide. So, it can be assumed that wet ESP can achieve even higher level of removal efficiency for ammonia as compared to hydrogen sulfide. In this regard, wet ESP technology seems quite promising for the control of malodorous emissions from CAFOs. Moreover as compared to other control technologies common in practice for similar purposes, wet ESP has proved to be technically sound and economically viable with better control performances. However more research has to be done with an emphasis to maximize the removal efficiency and hence promote and establish this technology as the standard technology for the control of CAFO emissions.

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A Biotrickling Filter for Removing Ammonia and Odour in Ventilation Air from a Unit with Growing-Finishing Pigs

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Abstract

The present study was carried out to investigate the ammonia and odour removal with a commercial biotrickling filter (SKOV A/S, Glyngøre, Denmark) in a unit with growing-finishing pigs. The results demonstrated that the filter significantly reduced the ammonia concentration (ppm) in the outlet air ($P<0.05$). Even though, the ammonia concentration before the filter ranged between 8.1 and 9.0 ppm during the winter period and 4.1 and 5.9 ppm during the summer period, the ammonia concentration after the filter was in the range of 1.2 to 2.4 ppm during the entire study. The filter significantly reduced the odour concentration (OU_E/m^3) in the outlet air ($P<0.05$). However, there were large variations in the odour removal efficiency, which ranged from an average of 54 % during the winter period and 28 % during the summer period. A possible explanation for the reduced odour removal efficiency during the summer was the increased ventilation rate, which reduced the retention time of the outlet air in the filter. It was observed that some areas on the filter were clogged up with dust and biofilm and this may also have impaired the odour removal. In conclusion, the filter was able to reduce the ammonia and odour concentrations in the outlet air from a unit with growing-finishing pigs. However, it is required to improve the odour removal efficiency and to find methods to increase the retention time and prevent the clogging with dust and biofilm.

Introduction

In recent years there has been a growing interest in reducing ammonia and odour from pig production in Denmark. In Denmark, the main research areas are reduction at the source, which means slurry and wet surfaces in the pig production unit and chemical and biological cleaning of ventilation air. A biotrickling filter is one of the promising methods for reducing both ammonia and odour from the ventilation air. It was reviewed by Melse and Ogink (2005) that biotrickling filters have a greater ability for removing odour compared with acid scrubbers, whereas acid scrubbers have a greater ability for ammonia removal. The present study was carried out to investigate the ammonia and odour removal with a commercial biotrickling filter (SKOV A/S, Glyngøre, Denmark) in a unit with growing-finishing pigs.

Methods

A unit for 416 growing-finishing pigs with partially slatted floor was used. The study lasted for one year and during this period four batches of pigs were produced. Two biotrickling filters were placed in two separated filter rooms in each side of the unit (filter rooms 1 and 2). The ventilation system was based on the principle of negative pressure ventilation. Fresh air entered the unit through a diffuse inlet in the ceiling. The outlet air was sucked out from the slurry channels and into ventilation channels under the solid floor in each side of the unit. The ventilation channels were connected to the filter rooms. The ventilation fan was placed on the clean side of the filter and the outlet air was drawn through the filter. The filter was composed by two vertical cellulose pads, which were continuously humidified with water. As the outlet air passed through the cellulose pads dust, ammonia and odour compounds in the air stream were degraded and metabolized by the biofilm on the pads.

Odour samples were collected in Tedlar® odour bags with a volume of 30 L. The bags were placed in an airtight container and filled by creating an underpressure in the airtight container by means of a pump. In each batch, four to six pair wise odour samples were taken from the air stream before and after the filter in filter room 1. Collection of odour samples and analyses of odour concentration (OU_E/m^3) took place in compliance with European olfactometric standard EN13725 (CEN, 2003). Ammonia concentration (ppm) was measured in the air stream before and after the filters using a Dräger Polytron 1 (Dräger Safety AG & Co. KGaA, Luebeck, Germany). The Dräger Polytron 1 was integrated in a VE 18 Multisensor

(VengSystem, Roslev, Denmark). The VE 18 Multisensor sampled at a flow rate of approximately 1-2 L/min and switched between outdoor air and the air stream before and after the filters. In the VE 18 Multisensor, sampled air was pre-heated to 34 ºC before entering the Dräger Polytron 1. The measurement of ammonia concentration was logged at 1 hour intervals. Every two weeks, controlling measurements of ammonia concentration were made with Kitagawa gas detector tubes 105SD (Mikrolab, Aarhus, Denmark).

Results and Discussion

Ammonia

In table 1, the average ammonia concentration in the air stream before and after the filters in the two filter rooms is shown. The ammonia concentration was significantly reduced in the filters ($P<0.05$). The ammonia concentration in the air stream before the filters ranged between 8.1 and 9.0 ppm during the winter period and between 4.1 and 5.9 ppm during the summer period. The ammonia concentration in the air stream after the filters was in the range of 1.2 to 2.4 during the entire study. Thus, it seems that the filters were able to reduce the ammonia concentration in the outlet air to approximately the same level despite the variations in the ammonia concentration in the air stream before the filters.

Table 1. Average ammonia concentration (ppm) in the air stream before and after a commercial biotrickling filter (SKOV A/S, Glyngøre, Denmark) in a unit with growing-finishing pigs. 95 % confidence limits are placed in brackets.

Batch	Period	Filter room 1		Filter room 2	
		Before	After	Before	After
1	14.10 - 13.12	9.0 (8.7 – 9.4)	1.2 (0.8 – 1.6)	8.2 (7.7 – 8.6)	1.3 (0.9 – 1.7)
2	07.01 - 22.03	8.1 (7.8 – 8.4)	1.8 (1.5 – 2.1)	8.3 (8.0 – 8.6)	1.6 (1.3 – 1.9)
3	28.05 - 29.06	4.1 (3.6 – 4.5)	2.2 (1.7 – 2.7)	5.9 (5.4 – 6.4)	2.4 (1.9 – 2.9)
4*	10.08 - 22.10	-	-	4.3 (3.8 – 4.7)	2.1 (1.6 – 2.5)

* In period 4, the hoses between filter room 1 and the ammonia analyzer were leaking and therefore data are not shown for this period.

Odour

In figure 1, odour concentrations are shown for all pair wise measurements before and after the filter in filter room 1. The odour concentration was significantly reduced in the filter ($P<0.05$). The reduction in odour concentration averaged 54 % during the winter period (95 % confidence limits: 45-63) and 28 % during the summer period (95 % confidence limits: 17-39). A possible explanation for the lower odour removal efficiency during the summer period was a reduced retention time in the filter due to the increased ventilation rate. A reduced retention time reduces the contact between the biofilm and the outlet air and thereby the odour removal. It was also observed that some areas on the cellulose pads were clogged up with dust and biofilm. The clogging with dust and biofilm may also have impaired the odour removal.

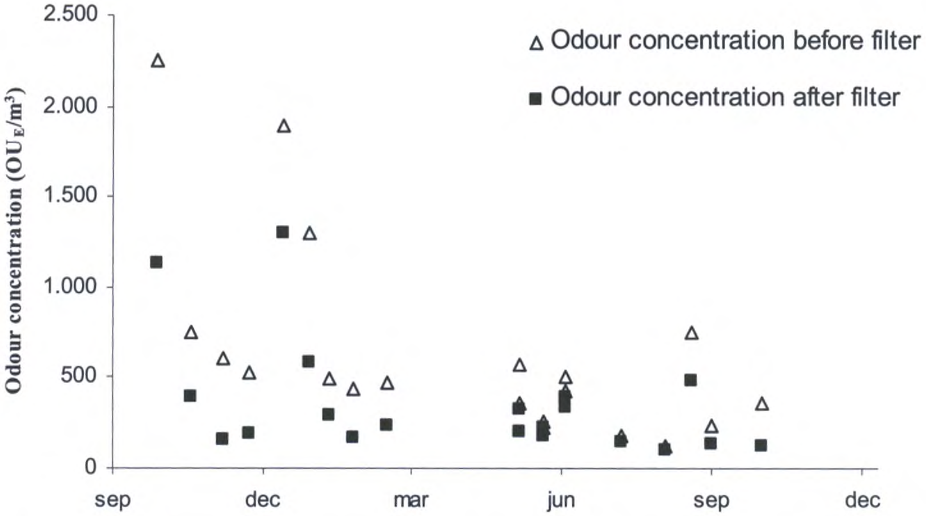

Figure 1. Odour concentration (OU$_E$/m^3) in the air stream before and after a commercial biotrickling filter (SKOV A/S, Glyngøre, Denmark) in a unit with growing-finishing pigs.

Conclusions

In conclusion, the biotrickling filter was able to reduce the ammonia concentration in the outlet air from a unit with growing-finishing pigs to approximately 1.2 to 2.4 ppm. The filter was able to reduce the odour concentration in the outlet air although the odour removal efficiency was higher in the winter period (54 %) compared with the summer period (28 %). The investigation demonstrated that it is required to improve the odour removal efficiency during the summer and to find methods to increase the retention time of the air in the filter and prevent the clogging of the filter with dust and biofilm.

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Unjustified Enforcement of Regulations Based on PM Emissions from Laying Hen Operations

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Abstract

The EPA press release dated 02/23/2004 entitled "Ohio's Largest Egg Producer Agrees to Dramatic Air Pollution Reductions from Three Giant Facilities" indicated that Buckeye Egg Farm, L.P., the largest commercial egg producer in Ohio, agreed to pay a civil penalty of $880,598 and committed to installing and testing $1.4 million of controls. EPA's justification for this action was that "Buckeye had failed to obtain necessary air permits" for their facilities at Marseilles, Mt. Victory, and Croton. The necessary permits were Title V and PSD (Prevention of Significant Deterioration). The PM_{10} stationary source emissions threshold (in an attainment area) for a facility to be classified as a "major source" and be required to obtain a Title V permit is 100 tons per year. The stationary source emissions threshold for a facility to be required to obtain a PSD permit is 250 tons of PM_{10} per year.

The EPA contractor's reported findings were analyzed and several serious errors were found. First, the consultants measured total suspended particulate (TSP) concentrations. These TSP concentrations were used in determining if Buckeye Egg Farm exceeded the thresholds for Title V and PSD permits. The reported particle size distribution of the particulate matter (PM) sampled and reported by the contractor demonstrated that the PM emitted was large with approximately 10% less than PM_{10}. EPA reported that the PM emissions from the three large laying operations were 740, 650 and 550 tons per year at Marseilles, Mt. Victory, and Croton, respectively. These values would have exceeded the thresholds, but the emissions were TSP, not PM_{10}.

It is incorrect to use annual TSP emissions to require Title V and PSD permits. In a memorandum from the Office of Air Quality Planning and Standards (OAQPS), USEPA, dated October 16, 1995, PM_{10} was specified as the designated regulated PM pollutant for Title V purposes. PM emitted from agricultural sources can be classified as large in size in comparison to PM emitted from urban sources. Typically, TSP from agricultural stationary sources is only 10 to 30% PM_{10}. Therefore, annual PM_{10} emissions, rather than TSP emissions, should be the criteria for requiring both Title V and PSD permits.

In addition, the EPA chose to calculate emissions assuming the 58 fans in each house were operating at an average of 14,000 cubic feet per minute (cfm) with no regard for ambient temperature. This assumption was made in determining the "potential to emit" for the facilities. This assumption was not an example of good engineering practice (GEP). It was inappropriate for EPA to use the high flow rate per fan for both cold and hot ambient conditions. The flow rate that EPA assumed would have likely resulted in the death of numerous birds. GEP should be used in determining annual PM_{10} emissions from agricultural stationary sources for the purpose of Title V and PSD permits. Using the consultant's report, which included the particle size distribution of the samples, it was determined that the amount of PM_{10} measured was a fraction of that reported. The PM_{10} emissions from all three operations did not meet the Title V permit threshold and therefore did not meet the PSD permit threshold.

The BlueSky Smoke Modeling System for Prediction of Smoke Impacts

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Abstract

BlueSky (www.fs.fed.us/bluesky) is a framework linking together weather prediction systems with the latest available fire science and air quality models to predict smoke concentrations from prescribed fire, wildland fire, and agricultural fire. The EPA Region 10 developed the sophisticated Rapid Access Information System (RAINS) user interface. Partnering these two systems led to the BlueSkyRAINS (BSR, www.blueskyrains.org) decision support system (DSS). The BlueSky system has been applied to many domains across the U.S. (northwest, California, Rocky Mountains, southeast and northeast) and internationally to Lisbon, Portugal. The BSR system has been applied to the northwestern and western U.S., and is in process for the southeast. In the northwestern U.S. the BSR system partners with Washington State University, who developed the ClearSky (http://clearsky.wsu.edu/) system, to address agricultural burning in eastern Washington State and northern Idaho. Agricultural burning is controlled and reported in a different manner than prescribed burning and wildfires, and the ClearSky system has been adapted to these differences by applying a scenario approach whereby regulators and land managers submit scenarios of likely burns for the next day. Evaluation of the BlueSky and ClearSky smoke prediction systems is a complex but critical task hampered by: paucity of observational data, background $PM_{2.5}$ concentrations from other anthropogenic and biogenic sources, secondary aerosol formation not taken into account by the Lagrangian model, uncertainty in plume rise calculations and dispersion methods, uncertainty in the predicted weather, and uncertainty in the emission estimation and fuel loadings. Measure of Success (MOS) methods are being investigated as well as available statistical evaluation measures. Finally, future work with the BlueSky and ClearSky systems will involve applying NASA satellite products for system initialization and evaluation.

Study on Deodorization of Spraying System in Pig Farms

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Abstract

Properties of nozzles would be analyzed in this study. Droplets size distribution of three kinds nozzles, 4002-5, 4002-8 and NO.3, were measured by Malvern 2600 Particle Size Analyzer. SMD, VMD and flexibility of maintenance were examined. Experimental results showed NO.3 nozzle is the best. Secondly, spraying system for the open type pig farm would be established. The distance between nozzles was 3 m, spraying pressure of the nozzle was 30 kg/cm2, spraying rate was 97.3 l/min, horsepower of motor was 5 hp. Finally, deodorization effect of spraying system applying to the open type pig farm would be studied. The effects of three kinds of spraying conditions, with water, attar, and non-spraying, were compared. Record of ammonia concentration was collected by weather station and odor concentration was measured by sensory evaluation were examined. The removing rate of ammonia concentration could be reached 52.9% and 13.9% for spraying with water and attar. The highest removing rate of odor concentration could be reached 78% and 62% for spraying with water and attar.

Introduction

Since peoples moving to the neighborhood of hog farms through country developing policy, the odor problems have become important issues in Taiwan. The methods were divided in two groups for preventing dispersion Firstly, the following arrangements could be applied for reducing the concentrations of odor from hog farms. They were planting tree around hog farms, increasing ventilation rate, increasing the frequencies of washing hog raising facilities, and spraying water fog or attar around the hog farms. Secondly, reducing the odor concentration of manure could be treated by changing the feedings of pig. Open-type pig farm with flexible plastic windows could be arranged to apply spraying system for deodorizing. The purpose of this study were as followings: measuring and analysis the droplet diameters and calculating the flow rate for 3 nozzles under 4 pressure settings; designing feasible spraying system for hog farms; finding the relationship between the meterologic parameters and deodorization effect of spraying system; suggesting the suitable operational model of spraying system for hog farms.

Methods

The flow chart of this study was arranged like fig.1. The methods and material were described according to it. Three nozzles were applied with model □3, 4002-5, and 4002-8 under four pressure setting with 20, 30, 40, and 50 kg/cm^2. They were evaluated by Particle Size Analyzer (Malver System 2600) for measuring the distribution of droplet diameters. Each pressure setting was measured three times and the averaged data will be presented. The flow rate of nozzles was calculated for establishing the proper spraying system for a hog farm with 1500 heads. Gas concentration detector (GV-100S) was used to measure the ammonia concentrations inside and outside hog building.

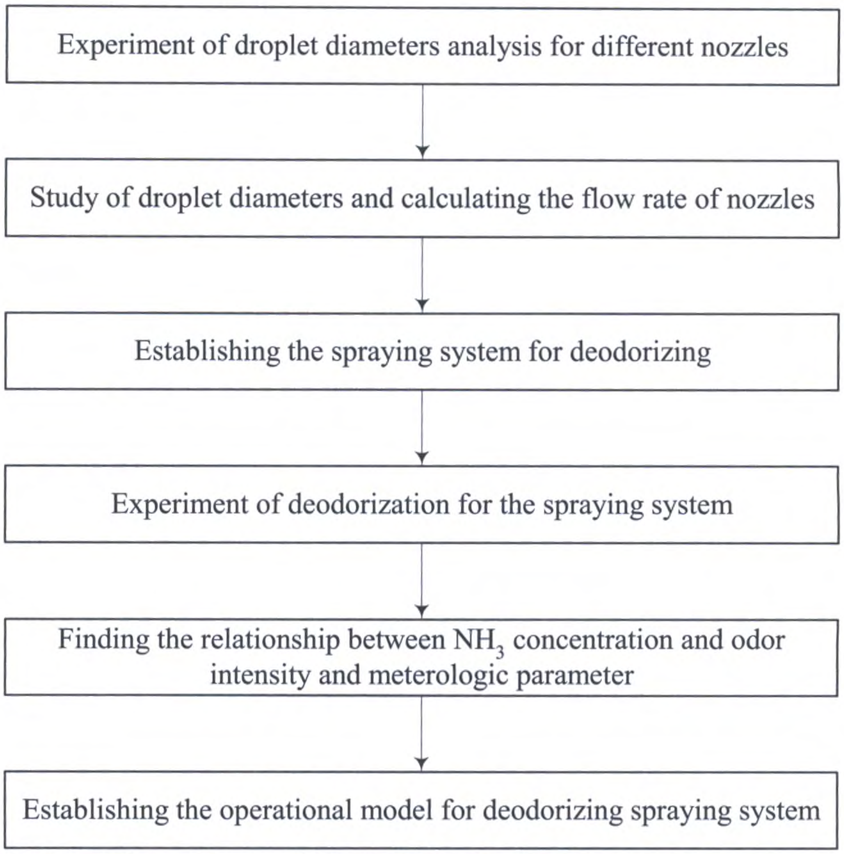

Figure.1 Flow chart of spraying system study for deodorizing.

Meterologic parameters were collected by data-logger system with the sensors of wind direction, wind speed, temperature, relative humidity, solar insolation and ammonia concentrations. Three operational model of spaying system were set as without water, with water and with attar. The deodorization effect were evaluated by sensory evaluation (olfactometer, odor intensity). Finally , the suitable operational model were projected for future study according to experimental results.

Results and Discussion

Table.1 shows the results of three nozzles under four pressure settings. Volume median diameter (VMD, μm) denotes the median diameter of droplets, Sauter median diameter (SMD, μm) denotes the averaged diameter of 43% accumulacted droplets and it is expressed as D43, and the flow rate of nozzle was calculated. VMD and SMD were decreased as the pressure setting increased. It followed the physical properties of spraying system. The flow rate was increased as the pressure setting increased. The experiment at farm had 1500 heads pigs and the ammonia production rate was evaluated as 22.4 l/min. Since the absorption rate of water to ammonia is 700, the flow rate of spraying system is determined as 32 ml/min. The arrangement of spraying system was showed like fig.2. The contact front between neighboring conflict and hog farm was 100 m long. There were 33 nozzles applied to the spraying system with a fogging pump (WL-60, 220V and 5hp) and an effective range of 3 m. The actual flow rate was 86.1 l/min (theorectical value as 97.3 l/min) under 30 kg/cm2 pressure setting. There were 2 storage tanks with the capacity of 2 tons which could provide the spraying system to operate more than 20 min.

Table.1 Droplet diameter analysis and flow rate calculation for different nozzles.

Nozzle type	Pressure(kg/cm^2)	VMD(μm)	SMD(μm)	Flow rate(ml/min)
#3	20	74.26	44.50	2421.5
	30	64.55	37.93	2948.0
	40	62.96	35.76	3428.0
	50	56.35	33.64	3828.0
4002-8	20	57.08	42.87	111.6
	30	52.60	38.38	140.6
	40	50.11	36.09	169.0
	50	47.09	32.74	188.6
4002-5	20	92.71	60.46	60.7
	30	74.00	41.05	84.7
	40	67.79	40.41	100.7
	50	65.77	38.59	121.7

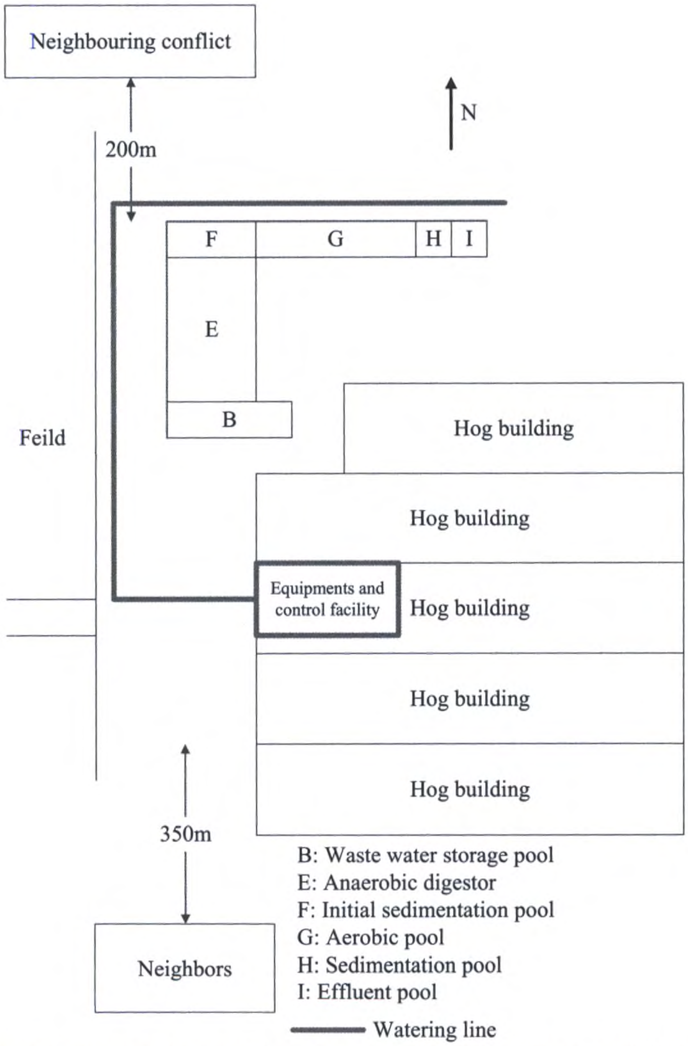

Figure 2. Arrangement of spraying system for experimental farm with 1500 pigs.

Fig.3 shows the relationships between wind speed and ammonia concentration inside the hog building for spraying system operated with water. It showed that the ammonia concentration was lower than 4.5 ppm while the wind speed was above 0.9m/s. Fig.4 and 5 showed the similar trendency for system operated under the conditions with attar and without water.

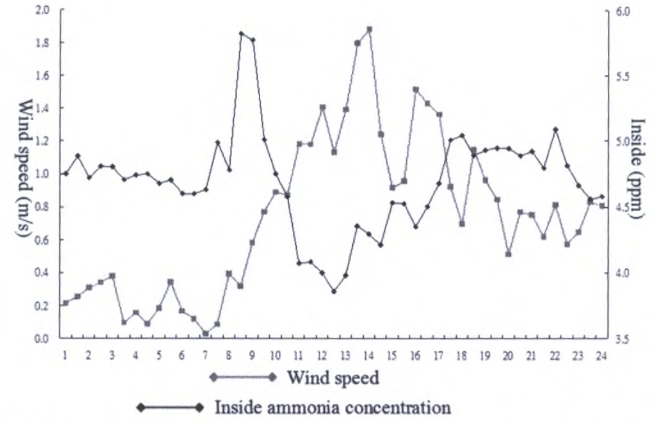

Figure. 3 Relationship between wind speeds and inside ammonia concentrations for the operation with water.

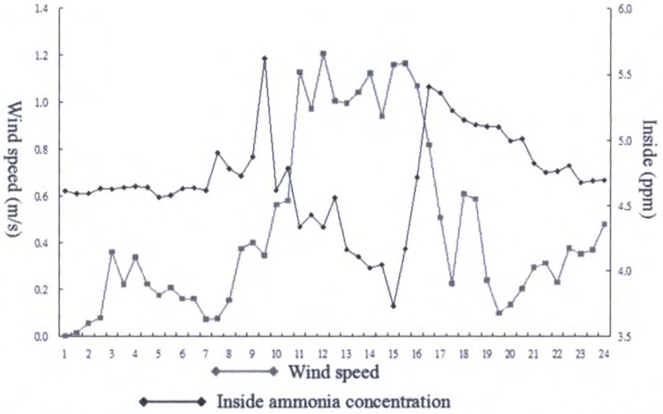

Figure. 4 Relationship between wind speeds and inside ammonia concentrations for the operation with attar.

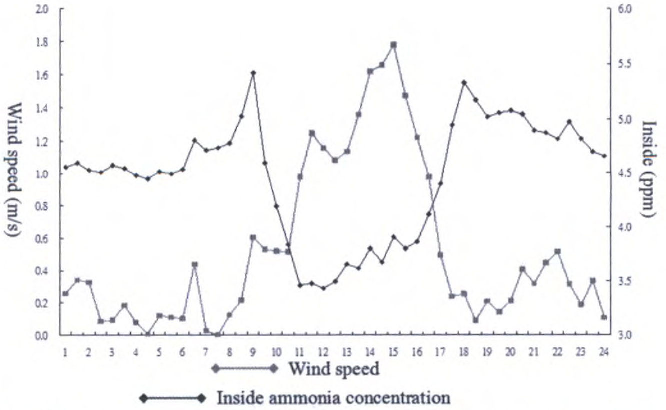

Figure. 5 Relationship between wind speeds and inside ammonia concentrations for the operation without water.

Fig.6 showed there was no significant difference among 3 operational settings for ammonia concentration inside hog building. But fig.7 showed there was similar trendecy among 3 operational settings for ammonia concentration outside hog farm. It implied that the concentration is lowest for the spraying system operated with water.

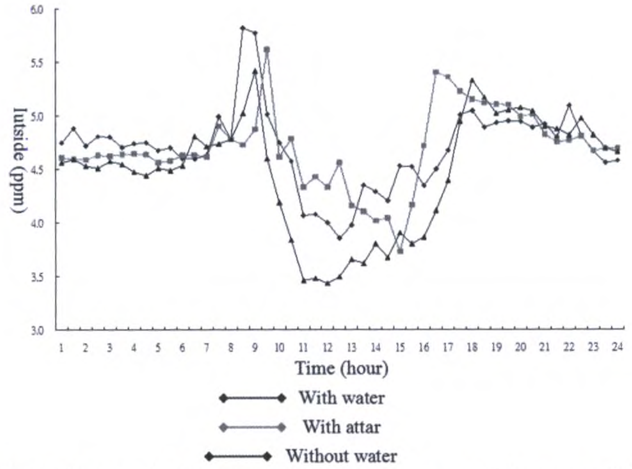

Figure 6. Relationship between iutside ammonia concentrations and time for three kind operations.

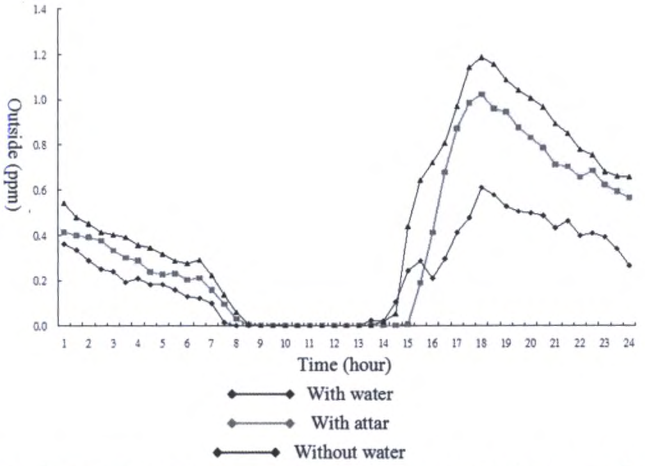

Figure 7. Relationship between outside ammonia concentrations and time for three kind operations.

Table.2 show the results of odor intensity (OU) and odor removing rate for different operations. There were 2 farms being evaluated and existing similar results. The odor removing rate could be reached like 78% for spraying system operated with water.The experimental results showed that spraying system can effectively reduce the odor from hog farm.

The following operational considerations were recommended like stopping the system while it rains, the wind speed is higher than 0.9m/s, and starting the system while the wind speed is lower than 0.9m/s for 30 minutes, the ammonia concentration inside hog building is higher than 4.5 ppm for 30 minutes, and the ammonia concentration outside hog building is higher than 1 ppm.

Table.2 Results of odor intensity (OU) for different operation.

Farm	Operation	Odor intensity (OU)	Odor removing rate (%)
A	No	100	
	Water	22	78
	Attar	38	62
B	No	100	
	Water	24	76
	Attar	41	59

Conclusion

Designing and field evaluation of spraying system were completed in this study for deodorizing of hog farm. The removing rate of odor could be reached to 78% with applying water fog. Further study should be conducted for long term operations and monitoring the neighboring reflection under varied weather conditions.

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Whole-Plant Regulation of Volatile Organic Carbon Emissions

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Abstract

The last 30 years have seen a revolution in our understanding of the controls over air quality. Improvements in measurement technology and modeling capability have combined with advances in scientific knowledge to allow detailed and accurate predictions of air quality from local to continental scales. Some of the most striking changes in our scientific knowledge have come from studies of the emissions of volatile compounds from plants to the atmosphere. Plants have been identified as major sources of photochemically reactive reduced organic compounds (known as Volatile Organic Compounds, VOC's), and the physiological controls over the emissions of these compounds are well understood. Incorporating these VOC's into tropospheric models of oxidant formation has improved markedly our ability to predict ozone dynamics across the Earth's surface. We present results from studies of VOC emissions from important agroforestry species, including Populus, Eucalyptus, Picea, and Pseudotsuga, which suggest that consideration of whole-plant ecological controls on emissions is essential for accurate models of VOC emissions. Environmental factors that affect VOC emissions act very differently on small plants growing in pots than they do on large trees in plantation forest settings, and whole-plant responses to these factors explain the differences. That is, physiological responses at the leaf scale may differ from ecological responses at the whole-plant scale. Specifically, damage to leaves, such as may be caused by herbivores, may cause increases in emissions from potted plants but decreases from large trees. Similarly, nitrogen fertilization can lead to an increase in emissions from saplings in greenhouses but no changes in emissions from large trees in agroforestry settings. These results highlight the need to consider ecological as well as physiological controls when developing VOC emission models that are to be used in air quality studies.

A Southeastern United States Site Characterization Involving Black Carbon Aerosol Concentrations and Meteorological Variables at an Agricultural Site, Raleigh, North Carolina

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Abstract

Aerosols present in the Earth's atmosphere play a crucial role in agricultural and global meteorological conditions. If there is a larger concentration of aerosols then there may be a resulting variance in the weather and climate. One particular aerosol, which was measured and observed for this study, is black carbon. The presence of black carbon concentrations could result in a variance of certain weather variables at any given location. Black carbon aerosols absorb incoming solar radiation, which can impact the vertical temperature profile. A comparison of results can be made between weather and climate conditions in which a significant amount of black carbon is present, and other conditions with minimal amounts of black carbon in the troposphere. The observed data analyzed is from the Lake Wheeler site, a semi-urban location near the threshold of the piedmont and coastal plain zones of central North Carolina. The period for evaluation is June 2003 through May 2004. The weather variables that were closely examined include air temperature, dewpoint temperature, relative humidity, wind speed, and wind direction. In addition, radiation data was collected and analyzed including solar radiation, photosynthetically active radiation (PAR), net irradiance, diffuse radiation and direct radiation. Aerosol optical depths (AOD), which are the measurement of light attenuation at specified wavelengths, were also collected and evaluated in both the ultraviolet and visible light spectrums. This was done in order to determine any relationships between black carbon concentrations and AODs at certain wavelengths. After examining the year's worth of data a site characterization involving the black carbon concentrations and meteorological variables for the Raleigh, NC location was devised. There are noticeable seasonal variations of black carbon aerosols at this agricultural site. Black carbon concentrations were the highest during the summer months of 2003, and lowest during the winter months of 2003-04. The primary cause of this variation is the regional wind regime and meteorological conditions that are present during each season. In the summer months the atmosphere over the southeastern United States tends to be more stagnant with high pressure often in control. In the winter months the atmosphere experiences dramatic changes throughout the season. Weather fronts frequently pass through the region causing large drops in temperatures. Fronts act as a cleanser of the atmosphere by transporting atmospheric contents further downstream. There are also daily variations of black carbon concentrations. These variations are mainly due to the vehicular travel habits of the residents of the southeastern United States, with higher concentrations occurring during the week when more individuals are commuting in their automobiles, to lower concentrations observed on the weekends due to less congested travel conditions.

The USDA UV-B monitoring research station places an emphasis on ultraviolet radiation measuring equipment, which is used in order for the USDA to assess the potential impacts of increasing levels of UV radiation on agricultural crops and forests. Two instruments, which are located in the open environment, include the Ultraviolet Multi-Filter Rotating Shadow band Radiometer (UV-MFRSR) and the Visible MFRSR. The UV-MFRSR measures the total horizontal solar irradiance in the ultraviolet spectrum at wavelengths of 300, 305.5, 311.4, 317.6, 325.4, 332.4 and 368 nanometers. This is accomplished by utilizing seven independent interference filter photodiode detector combinations. The visible MFRSR measures total horizontal surface irradiance in the visible spectrum at wavelengths of 415, 500, 610, 665, 862 and 940 nanometers. The visible MFRSR uses six independent interference filter photodiode detector combinations as well as a seventh channel, which is an unfiltered broadband silicon diode detector. Both instruments are used in order to determine the average optical depth. An UVB-1 Pyranometer is also located at the site. It measures the global irradiance in the UVB spectral range (280-330 nanometers). The station also has a Vaisala HMP 35A temperature and humidity probe which has a temperature range of -20 to +60 degrees Celsius and relative humidity range of 0-100%. A 210SZ LICOR photometer is pointed downward in order to measure the surface reflectance (albedo). Some additional instruments that are not standard USDA UV-B equipment but are located at the station include a Magee Scientific aethalometer, which provides a real-time and continuous measurement of the black carbon concentrations. Total scattering coefficients are also measured by using two nephelometers (set at different wavelengths). Sulfur dioxide, Nitrous oxide and Nitrogen dioxide concentrations are also measured and recorded at the Lake Wheeler site using Magee Scientific gas analyzers. The North Carolina Division of Air Quality maintains these supplemental instruments.

There have been previous studies involving black carbon aerosol concentrations that have been measured at various sites around the globe. Some of these investigations have found that an increase in black carbon concentrations near the surface of the Earth can lead to a decrease in temperature with an increase in absorption of incoming solar radiation by black carbon aerosols. Black carbon aerosols tend to absorb more incoming radiation in the visible spectrum than the ultraviolet spectrum. Aerosol optical depth and radiation measurements at seven different wavelengths for both the UV and visible spectrum were available for this study. Two wavelengths in the visible spectrum, 500nm and 610nm, and one wavelength in the UV spectrum, 332nm, were selected for comparison and analytical purposes for this particular study. Other chemically different aerosols such as sulfates can have a different effect on temperature and other meteorological variables if they are present. Sulfates tend to reflect incoming solar radiation versus the absorption effects of black carbon aerosols. Thus, if both aerosols are present at the same time in the same location their respective radiative qualities can counteract one another. Although sulfate aerosol concentrations were available for this time period and location, they were not examined for this individual study, which was intended to focus on the BC aerosols. Also, Nitrate aerosol concentrations and ozone concentrations were also measured and available at this station. Black carbon has a crucial effect on our environment and agricultural conditions, thus it is imperative to further examine this significant aerosol.

The Sensitivity of Fine Particle Mass and Its Chemical Constituents to NH_3 Concentration During an Intervention in Chicken Farming in the Lower Fraser Valley of British Columbia, Canada

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Abstract

Measurements of size resolved particulate inorganic and organic species were made with an Aerosol Mass Spectrometer in Abbotsford, British Columbia, Canada during the summer of 2004. Inorganic species including SO_4^{2-}, NO_3^-, NH_4^+ as well as total organics were measured in the ranges of 0.15 0.7ug m^{-3}, 0.05 0.6ug m^{-3}, 0.08 0.5ug m^{-3}, and 0.25 2.0 ug m^{-3} respectively. The organic fraction dominated the total particle mass (22.8 52.2 %), and was indicative of an aged and highly oxygenated regional aerosol. Simultaneous measurements of gas phase ammonia (NH_3) conducted at the site resulted in a mean concentration of 5.4 ppb, although levels as high as 50 ppb were observed. NH_3 accounted for much of the NH_X present (91.8% mean), easily neutralizing available inorganic acids and suggested that particle acidity was not sensitive to NH_3 concentration fluctuations. The sensitivity of $PM_{1.0}$ mass (determined by AMS), particle NO_3^-, NH_4^+, SO_4^{2-} and organic acids to NH_3 was shown to be linked to moderate NH3 levels but unresponsive at higher NH_3 concentrations. The point at which increases in NH_3 no longer have an effect on particle formation (transition point) was found to be dependent on the particulate species in question. The transition regions for NO_3^-, SO_4^{2-}, NH_4^+, total organic acids and PMAMS were determined to be at NH_3 concentrations less than approximately 10.3, 4.5, 7.0, 6.0 and 6.5 ppb respectively. The sensitivity of particle NO_3^- (~6.3×10^{-4} umol m^{-3} ppb^{-1} NH_3) at the mean NH_3 levels was significantly higher than the corresponding sensitivity for SO_4^{2-} (~1.7×10^{-4} umol m^{-3} ppb^{-1} NH_3) and suggests that some degree of control over particle formation in this region is possible by reducing ambient NH_3 levels. This would primarily involve a decrease in particle NO_3^- formation while SO_4^{2-} would be largely unaffected.

Workshop on Agricultural Air Quality

Effect of Litter Moisture Content on Ammonia Emissions from Broiler Operations

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Extended Abstract

Livestock production buildings such as broiler houses represent a major source of ammonia emissions, and exposure to high level of ammonia can be detrimental to the health and performance of poultry. This study will investigate the characterization of ammonia emissions from broiler litter, and especially, the effect of litter moisture content on ammonia fluxes.

The mechanisms related to ammonia emissions from litter based manure include several processes: hydrolysis of urea, enzymatic and microbial generation of ammonia, partitioning between solid phase and aqueous phase ammonia, the chemistry of ammonia in aqueous solution, partitioning between solid/aqueous phase and gaseous phase ammonia, and the convective mass transfer of ammonia gas from the surface into the free air stream. In the litter-air system, the ammonia equilibrium and production rate can be influenced by many factors, such as temperature, pH, nitrogen content and moisture content of litter material.

In practice, litter moisture is mainly influenced by ventilation and drinking system management. It has been reported qualitatively that wet litter can lead to high ammonia levels in broiler housing and may cause bird health problems such as hock burn. Litter moisture may affect ammonia emissions from litter in many ways. First, it may affect the conversion rate of uric acid to ammonium-N. It may also influences the microbial and enzymatic activities, partitioning and diffusions of ammonia as well as the chemistry of the solution in the system. Overly dry litter may result in more dust particulates which serve as a transport mechanism for ammonia. The comprehensive effect of litter moisture content is complex and still not well known.

Current studies on ammonia emissions from broiler litter have largely focused on measuring ammonia emissions from individual broiler production systems. As a lot of uncertainty exists due to specific local conditions and technical challenges in the field measurements, it would be valuable to develop an apparatus and experimental procedure that allow the measurement of ammonia flux from broiler litter under controlled conditions. Under lab controlled conditions, quantitative relationships between ammonia emissions and controllable parameters (such as litter moisture) can be obtained with more confidence and better understanding. The results would be important in developing emission models in terms of management practices and environment conditions so that ammonia emissions from broiler litter can be predicted under given conditions. Better understanding of the relationships between ammonia emissions and controllable parameters would also be helpful in the effort of searching better management practices (e.g. litter management, drinker systems and ventilation systems) and/or designing practical and cost effective strategies to control ammonia emissions from broiler houses.

The research objectives of this study include:

(1) Develop an apparatus and experimental procedure that allow the measurement of ammonia flux from broiler litter under controlled conditions;

(2) Measure and characterize the ammonia flux from broiler litter, develop a model that can describe and explain the comprehensive effect of litter moisture content on ammonia emissions;

The long term objective is to develop a process based mechanistic emission model for broiler litter, which will address the influence of various management practices on ammonia emissions.

A dynamic flow-through chamber system is designed for measuring and characterizing ammonia emissions from broiler litter. A vacuum pump draws air through the chamber at a constant flow rate via flow controllers (Gilmont Shielded Industrial Flow meter, accuracy ±5%). Before enter the chamber, ambient air passes through a carbon filter so that any background ammonia is removed. The air inside the chamber is mixed by a variable-speed, motor driven stainless steel impeller. The dynamic chamber system, with the continuous stirring provided by the impeller, meets the necessary criteria for performance as a continuously stirred tank reactor (CSTR). Trace experiments (residence time distribution) has been used to test the flow and mixing characteristics of the system with the similar design, and the results of these mixing studies indicated that the dynamic chamber behaved as a “perfect” mixer with negligible stagnancy or channeling. The entire chamber body is made of stainless steel and Teflon tubing is used to minimize the loss of ammonia.

Broiler litter samples will be put into the dynamic flow-through chamber and ammonia free air will be directed into the chamber and to pass over the samples to promote convective conditions similar to that in a typical broiler houses. Concentration of ammonia inside the chamber will be measured with a Thermo Environmental Instruments (TEI) chemiluminescence ammonia analyzer (Model 17C). A parallel sample will be taken by wet scrubber (acid trapping) to measure the weighted- average ammonia loss from litter, and it can also work as a quality check for TEI measurements. Ammonia fluxes will be calculated using the mass balance approach. Before the test, litter samples will be dried in desiccate cabinet or treated with water to achieve different levels of moisture content. During the test, litter moisture content will be measured continuously with an ECH2O moisture sensor (EC5). A temperature sensor will be used to monitor litter temperature. A data logger (EM50) will be used to record the moisture and temperature data. The pH value of litter samples will be measured at the beginning and at the end of each test run.

Data of ammonia flux, pH, litter temperature, and litter nitrogen content at different levels of litter moisture content will be analyzed using the SAS statistical package to develop regression models for litter moisture content and ammonia flux. The optimal litter moisture content will be explored to prevent ammonia emissions. Also, the covariance between litter moisture content, pH, litter temperature, and litter nitrogen content will be analyzed.

The results of this study will provide a better understanding of effect of litter moisture content on ammonia emissions, which may be important for better broiler litter management (e.g. drinker systems) and will be helpful in designing practical and cost effective strategies to control ammonia emissions from broiler houses.

Keywords: Ammonia emissions, Broiler litter, Moisture content, Dynamic flow-through chamber

Characterization of Odors, Volatile and Semi-Volatile Compounds emitted from Swine Manure using Solid Phase Microextraction and Multidimensional Gas Chromatography – Mass Spectrometry - Olfactometry

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Abstract

Swine operations are associated with emissions of odor, volatile organic compounds (VOCs) and other gases. One of the major sources of VOCs and odor is the manure. However, relatively little is known about VOCs and gases emitted and their relationship to the malodor. It is critical to characterize swine manure VOCs and malodorous gases to improve the understanding of the environmental impact of swine operations. This knowledge is also needed to develop and evaluate odor and gas emission strategies and technologies. In this research, solid phase microextraction (SPME) and multidimensional gas chromatography-mass spectrometry-olfactometry (MDGC-MS-O) system were used to identify VOCs and other gases emitted from swine manure. This analytical system enables simultaneous chemical and sensory analyses of air samples. Manure were collected in jars from the Swine Nutrition and Management Research Farm and transferred into individual vials in the Atmospheric Air Quality Laboratory. Gas samples were extracted from vial headspace using Carboxen/Polydimethylsiloxane (PDMS) 85 μm SPME fibers and were analyzed using the MDGC-MS-O system. Twenty four hours SPME extractions were used to improve the method detection limits for semi-volatile organics and compounds with small affinity to SPME fiber coating. The MDGC-MS-O system was equipped with two columns in series with a system of valves allowing transfer of samples between them (heartcutting). Thirty-second-wide heartcuts were used to maximize the isolation, separation and identification of compounds emitted from swine manure (Figure 1). The odor impact of separated compound was evaluated by a trained panelist using the sniff port and Aromatrax odor characterization software. Odor was evaluated for character and intensity.

To date, 305 compounds with molecular weights ranging from 34 (H_2S) to 268 (pristane) were identified using analytical software BenchTop/PBM and MS Chemstation. Fifty eight compounds were positively confirmed with standards. Eighty three compounds had a distinct odor/aroma and several had a strong impact on the characteristic swine odor. Sixteen were classified as hazardous air pollutants (HAPs). The correlations between compounds emitted from swine manure were studied. Physical and chemical properties of each compound such as carbon number, boiling point, vapor pressure, water solubility, octanol-water partitioning coefficient (logKow), atmospheric lifetime based on reactions with OH• radicals (τ) and odor characteristics were summarized.

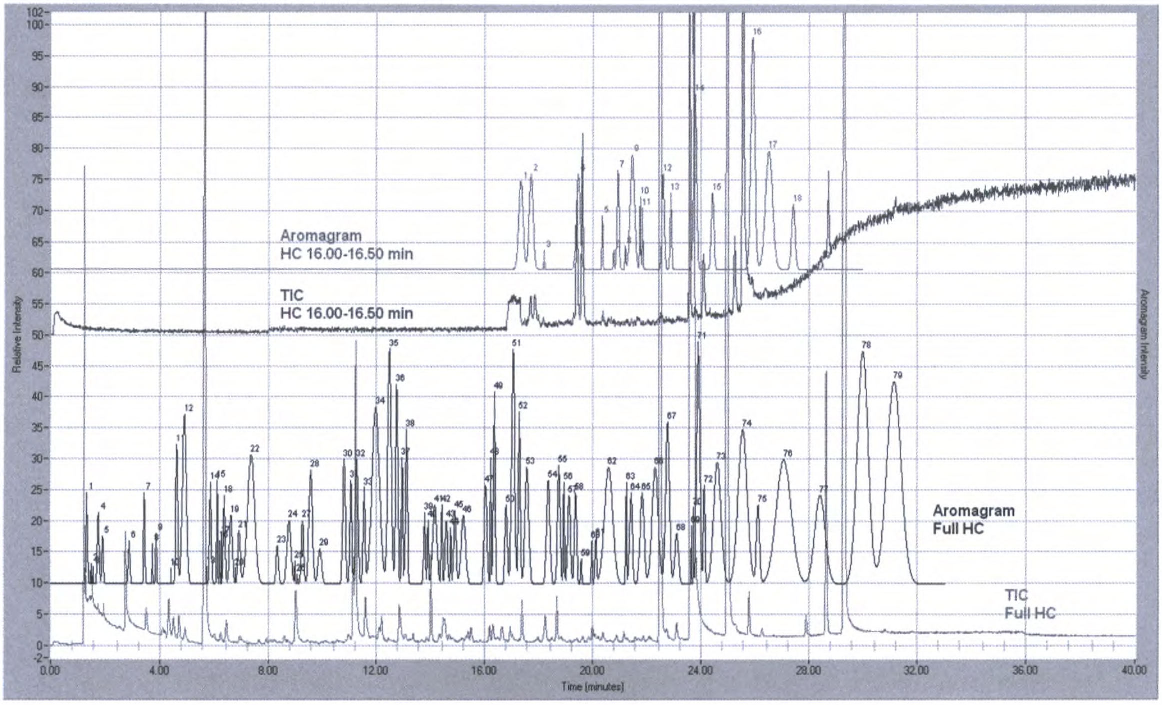

Figure 1. Chemical and sensory analysis of gases emitted from swine manure. Sampling and sample preparation was completed with a Carboxen/Polydimethylsiloxane (PDMS) 85 µm SPME fiber and analyses were completed on a multidimensional GC-MS-Olfactometry system. Top two lines represent an aromagram and total ion chromatogram (TIC) of isolated and separated compounds of a heartcut from 16.00 min to 16.50 min in multidimensional mode. The same chromatographic region is shown as a narrow and poorly separated band on the bottom line.

Assessment and Comparison of Annual Gaseous Emissions of Three Biological Treatments of Pig Slurry with a Storage-Spreading System

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Abstract

Field measurements of ammonia (NH_3), nitrous oxide (N_2O), methane (CH_4) and carbon dioxide (CO_2) were carried out from biological aerobic treatment plants installed in Brittany (Western France). Three biological aerobic reactors and four treatment by-product storages were studied. The field results showed that the emissions of CH_4, CO_2 and NH_3 were more important for the non-aerated effluents (raw slurry and separated solid fraction), which have higher ammonium and organic matter levels than treatment by-products. N_2O was only detected from biological reactor and was lower than 1% of total nitrogen entering treatment plant. The assessment and calculation of annual gaseous flux based on these field results and an estimation of raw slurry, matter flows and gaseous emissions for each module of the treatment was done for 4 slurry management schemes for a farrowing-fattening farm with 200 sows. In all cases, the environmental assessment shows a decrease of the greenhouse gases and NH_3 by using a biological treatment compared to a traditional manure management based on 6 months storage before spreading. The reduction is 30-50% to 68 % of NH_3 when the plant is or not set up with a mechanical separation device. Greenhouse gases are reduced by about 55% whatever the biological treatment plant.

Introduction

In France biological aerobic treatment is proposed as a management alternative for pig slurry farms whose the amount of applied nitrogen from animal manure is higher than the level of the EC Nitrates Directive (170 kgN/ha and year). At present, about 250 to 300 pig slurry treatment plants are in operation, mainly in Brittany. Among these plants, biological treatment using intermittent aeration concerns 80% of the existing plants. Biological aerobic treatment transforms a part of the nitrogen load in gaseous compound (mainly N_2) by nitrification and denitrification processes (Burton et al, 1993; Beline et al, 1998). Nevertheless, slurry nitrogen transformation and nitrogen transfer into the atmosphere could produce polluting gaseous emissions such as nitrous oxide (N_2O) and ammonia (NH_3). In the same way, the storage of the treatment by-products (aerated liquid manure, solid separated fraction, biological sludge and supernatant) could be a source of different pollution transfers into the atmosphere. Indeed, the manure management lead to gaseous emissions mainly NH_3, CH_4, N_2O, and CO_2. (De Bode, 1990; Husted, 1994; Sommer, 1991). These gaseous emissions depend on various parameters such as volume and composition of manure, type and time of manure storage and climatic conditions (temperature, wind velocity, …). For raw slurry storage the available data place the ammonia emissions between 1.8 and 12 gN/m^2 and day (De Bode, 1990; Sommer et al, 1993; Loyon et al, 2004) while carboneous emissions (CH_4, CO_2) varied between 0.4 and 70 gC/m3 and day (Husted, 1994; Zeeman, 1994; Safley and Westerman, 1988; Martinez et al, 1999). For biological treatment using intermittent aeration available data concern principally the reactor. Ammonia emissions depend on the residence time and are very low (Evans and Smith, 1986; Burton, 1992; Beline et al, 1998). Nitrous oxide emissions from intermittent aeration system are evaluated at 2-3% of total nitrogen (Osada et al, 1995; Beline and Martinez, 2002; Melse and Verdoes, 2005). The aim of the study was to evaluate the annual gas flow of biological treatment systems by (i) measuring on site the emissions of NH_3, N_2O, CH_4 and CO_2 of different modules of 3 biological treatment units (raw slurry pit, reactor, aerated slurry separation and by-product storages) and (ii) comparing annual gas flow of three biological treatment plants with traditional manure management based on storage before spreading.

Methods

NH_3, N_2O, CH_4 and CO_2 were measured under field conditions for 6 modules of storage or treatment modules: (1) raw slurry storage before spreading, or before treatment, (2) biological aerobic treatment by 3 means of aeration (surface aerator, fine-bubble diffuser, submerged ejector aerator), (3) solid separated fraction storage from decanter centrifuge or compacting screw, (4) aerated slurry separation by decantation, (5) biological sludge storage and (6) supernatant storage. Gaseous emissions from aerobic reactors and from storages of raw slurry, aerated slurry, supernatant and biological sludge were measured using the dynamic chamber technique (Peu, 1999). Gaseous emissions during storage of solid separated fractions were measured by enclosing the heap in a large polyethylene structure drawn up by a wind motor. The concentrations of CH_4, CO_2 and N_2O were measured either by infrared detection (analyser URAS 14 and 10) or by FID/ECD gas chromatography (Varian star 3800). Ammonia concentration was determined by using trap bottles filled with sulphuric acid (0.5 N) followed by a distillation and a titration. The gaseous measures were carried out for 4 to 7 weeks at different seasons (Table 1). All liquids and solid effluent were sampled weekly and analyzed for the principal characteristics (total ammonium nitrogen, total nitrogen, chemical oxygen demand, total solids, total suspended solids). Gas emission flows were estimated on a step of daily time by applying the field experimental gaseous factors to the various product storages. A simulation of the raw slurry characteristics, matter flows and gaseous emissions for each module of different treatment units was done with a Visual C++6.0 program for a « farrowing-fattening » farm with 200 sows. Volume and characteristics of slurry from the different housings used for the simulation of raw slurry to be treated or stored come from Levasseur (1998, 2002) while biological treatment by-products flows were based on field measurements (Beline et al, 2004). Gas emissions flows were calculated for three biological treatment plants and compared with a traditional manure management based on storage before spreading. The three biological treatment plant differed only by the mechanical separation (Table 3).

Results and Discussion

Experimental gas emission factors of CH_4, CO_2, NH_3 and N_2O and main characteristics of raw slurry storage, treatment reactors and by-product storages are presented in Table 1 and 2. As expected field results show that biological treatment has an impact on manure characteristics. Solid separated fractions (SSF) have a higher ammonium and organic matter level than raw slurry (RS), which reflects a higher dry matter content. Generally, all aerobically treated effluents have a lower concentration of ammonium and organic matter due to the biological decomposition of the organic matter. The difference on chemical characteristics not surprisingly affects the gaseous emissions (Table 2). The higher the ammonium and organic matter level of the effluent, the higher the emissions of NH_3, CH_4 and CO_2. Thus, with higher levels of TAN and TVS (about 4 gN/kg and 270 g/kg) than those for raw slurry (2.8 gN/kg and 30 g/kg) the solid separated fraction emitted more NH_3, CH_4 and CO_2. Gaseous emissions were for the solid separated fraction around 26-29 gN-NH_3/T and day, 50-54 gC-CH_4/T and day and 760-1170 gC-CO_2/T and day and for the raw slurry 4-6 gN-NH_3/m^2 and day, 50-57 gC-CH_4/m^3 and day and 41-45 gC-CO_2/m^3 and day. High production of CH_4 and CO_2 of solid separated fractions is due to high concentration of biodegradable organic matter. During slurry aeration NH_3 emissions were undetected due to high residence time of the slurry in the reactor (>30 days) (Evans and Smith, 1986; Burton, 1992; Beline et al, 1998). Moreover emissions of CH_4 were low (0.1-0.9 gC-CH_4/m^3 and day) and these minor emissions only occurred during anoxic stage allowing degradation of organic matter. This biological transformation also inevitably produced CO_2 (4-17 gC-CO_2/m^3 and day). Nitrous oxide was measured only during biological aerobic treatment. Indeed, manure storage under liquid form and anaerobic conditions is not favourable to nitrous oxide production (Osada et al, 1998 ; Phillips et al, 1997). Nitrous oxide emissions occur with nitrification/denitrification processes under both aerobic and anaerobic conditions. Whatever the type of aerator nitrous oxide emissions are low, less than 1% of the total nitrogen entering the treatment plants. These results are in accordance with the literature values (Osada et al, 1995; Beline and Martinez, 2002; Melse and Verdoes, 2005).

Table 1: Characteristics of pig slurry and biological treatment by-products (Mean values) (NM: not measured)

	RS_1	RS_2	SSF_1	SSF_2	BAT_1	BAT_2	BAT_3	ASS	BS	S
Season	Sum.	Aut.	Wint.	Wint.	Spring	Wint.	Sum.	Spring	Aut.	Sum./Wint.
Total Ammoniacal Nitrogen (TAN, gN/kg)	2.5	2.8	4.9	3.8	2.6	2.4	2.5	0.2	0.2	0.05
Total Nitrogen (gN/kg)	4.0	4.0	11.0	7.6	3.9	3.2	3.7	1.2	1.7	0.2
COD (gO_2/kg)	61	44	353	332	NM	26	45	19	32	2
Total Solids (g/kg)	49	42	340	306	30	22	42	22	34	7
Total Volatile Solids (TVS, g/kg)	34	30	268	265	19	13	30	10	14	1

RS_1, RS_2: raw slurry storage with and without mixing, SSF: storage of solid separated fraction (1: centrifuge, 2: compacting screw), BAT: biological aerobic treatment (1: surface aeration, 2: fine bubble aeration, 3: hydroejector), ASS: aerated slurry decantation, BS: storage of biological sludge S: storage of supernatant

Compared to the traditional slurry management, the biological treatment seems less pollutant in terms of NH_3 and CH_4 (Table 3, Figure 1). Annual gas flow estimation shows that biological treatment with or without separation can reduce NH_3 emissions by 30-50% and 68% respectively. The CH_4 emissions are reduced by around 70% whatever the treatment.

Table 2: Field measures of gaseous emissions (Mean values, ND: no detection)

	RS_1	RS_2	$SSF_1{}^1$	$SSF_2{}^1$	BAT_1	BAT_2	BAT_3	ASS	BS	S
Season	Sum.	Aut.	Wint.	Wint.	Spring	Wint.	Sum.	Spring	Aut.	Sum./Wint.
NH_3 (gN/m^2 and day)	4.1	6.7	26.1	28.9	ND	ND	ND	0.16	0.26	0.25
N_2O (gN/m^3 and day)	ND	ND	ND	ND	0.015	0.58	0.27	ND	ND	ND
CH_4 (gC/m^3 and day)	56.9	49.8	53.4[1]	50.4	0.87	0.13	0.09	7.6	5.6	0.62
CO_2 (gC/m^3 and day)	44.5	41.9	762.7	1170	12.1	16.9	4.1	4.8	6.7	0.35

[1] Emission values for solid given as grams/day per tonne rather than per m^3

RS_1, RS_2: raw slurry storage with and without mixing, SSF: storage of solid separated fraction (1: centrifuge, 2: compacting screw), BAT: biological aerobic treatment (1: surface aeration, 2: fine bubble aeration, 3: hydroejector), ASS: aerated slurry decantation, BS: storage of biological sludge S: storage of supernatant

Table 3: Estimation of annual gaseous flows of traditional and 3 biological treatment units

		NH_3	N_2O	CH_4	CO_2
Management	Description	kgN	kgN	tC	tC
Traditional system	RS_2	824	0	14.7	11.5
Treatment unit 1	RS_1+ ABT_2+ AS+BS+S	265	139	4.2	7.6
Treatment unit 2	RS_1+ SSF_1 +BAT_2+ ASS+BS+S	577	121	4.7	16.3
Treatment unit 3	RS_1+ SSF_2 +BAT_2+ ASS+BS+S	392	133	4.3	12.6

RS_1, RS_2: raw slurry storage with and without mixing, SSF: storage of solid separated fraction (1: centrifuge, 2: compacting screw), BAT_2: aerobic biological treatment by fine bubble aeration, ASS: aerated slurry decantation, S: storage of supernatant, BS: storage of biological sludge

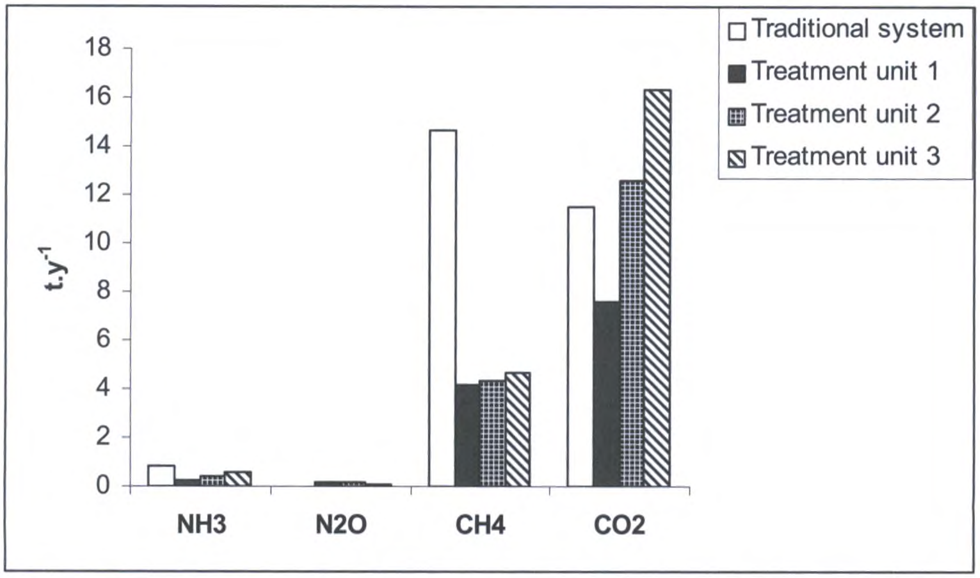

Figure 1: Estimated annual gaseous flow for four slurry management systems

Conclusions

This study underlines the influence of effluent composition and management method on the resulting gaseous emissions. The higher the ammonium and organic matter levels, the higher the emissions of NH_3, CH_4 and CO_2. The emission rates obtained in this study reflect mainly the difference in the effluents and their treatment but it is noted that environmental conditions (especially temperature) also have an effect. However it is the manure characteristics which is the main parameter influencing the methane and ammonia emissions. Under favourable conditions (temperature, pH and low redox value), the production of CH_4 is a function of the content of degradable organic matter while the NH_3 volatilization is a function of the total ammoniacal nitrogen. The higher these parameters, the more important the emissions of CH_4 and NH_3. The aerated products when stored emitted less polluting gases than raw slurry. Compared to traditional slurry management (storage + spreading), biological treatment seems less pollutant in terms of NH_3 and CH_4. Annual gas flow estimation shows that biological treatment with or without separation can reduce NH_3 emissions by 30-50% and 68% respectively. The CH_4 emissions are reduced by around 70% whatever the treatment.

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Compositional Identification of Odor Causing Compounds in a Dairy Farm

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Abstract

Obnoxious odorous emission from confined animal feeding operations (CAFOs) such as swine, poultry and dairy farms, etc. is the rising air pollution problem that not only causes nuisance in the neighboring community but also poses public health threats. This issue represents a typical air pollution problem due to lack of specific legislative controls. Moreover the researches in this field are still at the development stage owing to the limitations in sampling and instrumentation techniques. This research is aimed at the innovative use of the high volume sampling technique with sorbent cartridges to collect the odorous emissions from CAFO farms at representative locations. The series of sorbents of the sampling system was custom designed to better target the volatile organic compounds in such facilities. The high-vol sampling method was validated in the lab for its performance by sampling artificial swine odor sample. Sampling of odorous emissions using the high-vol sorbent based sampling system was followed by the identification and characterization of the odor constituents utilizing chromatographic technique such as GC-MS. The preliminary results on the organic odor compositions have proved the applicability of this method for sampling obnoxious emissions in CAFOs. However more research is required in this aspect to improvise the sampling technique so as to enhance its performance for collecting odorous emissions from animal facilities and to characterize the odorous emissions as per the emission sources in such animal facilities.

Introduction

Odorous emissions from confined animal feeding operations (CAFOs) have raised serious concerns more than ever due to the increased industrialization of these facilities.

Odor emissions cause nuisance in the community because of the persistent repulsive smell [1], and moreover, it poses potential risks to public health. The major air pollutants emitted from CAFOs include gaseous pollutants such as ammonia, hydrogen sulfide, nitrous oxide, methane and volatile organic compounds and particulate matter (PM). Studies have established direct correlation between the health impacts among the workers in the animal farm houses and the emission level of hazardous gaseous pollutants in such facilities, which demonstrated the needs for appropriate remedial actions.

There have been ample of studies regarding ammonia and hydrogen sulfide emission from the animal facilities [2-3] whereas the odor emission from CAFOs, however, is the least understood despite its overwhelming aesthetic and health impacts at the community level. The odorous emissions (in addition to ammonia and hydrogen sulfide) generally consist of VOCs (volatile organic compounds) such as aldehydes, aromatic hydrocarbons, volatile fatty acids (VFA) and compounds containing nitrogen and reduced sulfur [4-6].

In terms of measuring odor, dynamic dilution olfactometry measurements have long been employed to determine the character and the strength of the unpleasant smell [7]. This method only provides an overall odor result without specific information as to what chemicals invoke the odor. It is therefore inadequate for understanding the cause of the odor and in turn insufficient to come up with the ideas for the development of effective control technologies. Besides being labor intensive and expensive, this method also has human subjectivity involved.

Literature review shows that for the purpose of collecting and identifying odorous emissions from animal facilities, sampling is carried out in gas absorption cartridges with micro flow rates i. e. less than 1 liter per minute followed by thermal desorption techniques for chromatographic analyses. Razote et. al. in his research used solid phase micro-extraction (SPME) fiber for air sampling [8]. The flow rate was very low (100ml/min) and only compositions with high concentrations (from 960 ppm to 19 ppm) were detected.

The SPME technique also requires a special injector on the GC (gas chromatography) and can be affected by the desorption properties of the compositions from the fiber.

Zahn et. al. established a synthetic swine odor containing 19 different compounds, including volatile fatty acids and other volatile aromatic compounds to mimic the odor in the swine facilities [9]. The formulation of the synthetic swine odor was a significant contribution with respect to odor sampling and detection, and it also offers a tool to validate new sampling method and analytical techniques.

In order to overcome the drawbacks associated with the above mentioned sampling methods, an innovative sampling methodology was developed in this research. **The central hypothesis is that the resolution of low concentration compounds can be improved by collecting a large amount of air sample, and with high-volume sampling, the collection time can be shortened.** Although not used in agricultural settings, sampling in much larger volume (30 L/min or more) have been performed in source sampling applications such as wood combustion, diesel truck emissions and cigarette smoke, using sorbent cartridges, such as PUF(polyurethane foam) and XAD. The gaseous components can then be extracted with organic solvents and analyzed using GC-MS (gas chromatography and mass spectroscopy).

Experimental Approach/ Methods

The sampling system comprises following components:

Sampler Design

The sampling system comprises of a high volume vacuum pump that can draw air through at the rate of up to 300 liters per minute. The gas cartridge holder sits above the pump and below the filter holder. The gas cartridge consists of a cylindrical glass insert in which adsorbent material is placed with a wire screen to support the adsorbent. There are ports across the filter holder as well as the cartridge holder to measure the pressure drops across the filter and the cartridge.

Adsorbent Materials

Silica gel, XAD resin and Charcoal were selected as adsorbent material along with the polyurethane foam (PUF) because of their well known capability of adsorbing polar compounds such as acids and non acids, semi-volatile and volatile compounds respectively. Initially approximately 10 grams each of charcoal, silica gel and XAD were packed in the glass holder (6 cm by 7.6 cm) in the order as written and were separated by slices of PUF plugs, approximately ½ inch thick in between these sorbents. The PUF plugs were also kept at the front and the back ends of the glass holder. The front PUF was 1 inch thick as compared to ½ inch thick PUFs in the middle as it was assumed to trap more compounds being at the front. The whole sorbent assembly was wrapped in aluminum foil, sealed in a plastic bag and kept inside the refrigerator to prevent any contamination. Besides these, particles were removed by the baked quartz filter paper placed in the filter holder of the sampler.

Among different adsorbents used in the sorbent assembly, XAD was the purified form of Amberlite XAD-2 Resin purchased from ‘Sigma Aldrich’ along with Silica gel and PUF. It is commonly used while monitoring semivolatile organics ambient contaminants because of its affinity to such compounds. It has its application in several US EPA methods such as SW-846 Method 0010, “Modified Method 5 Sampling Train for Principal Organic Hazardous Compounds (POHCs)”; TO-13 – “PAHs in ambient air”; IP-7 – “PAHs in indoor air”, etc.

Likewise several US EPA and ASTM methods require polyurethane foam (PUF) adsorbent cartridge for monitoring semivolatiles in ambient, indoor, and workplace atmospheres. The advantage of using PUF as a sampling sorbent in this research is the low pressure drop. It finds its application in standard methods such as ASTM 8461, for the collection of pesticides and PCBs, EPA TO 9A for the collection of dioxins, etc.

McGinn et. al, had used activated silica gel in a small tube and was able to capture 7 volatile fatty acids (acetic, propionic, butyric, isobutyric, valeric, isovaleric and caproic) and other non acidic compounds such as phenol, skatole, indole, p-cresol, etc. from the ambient air near beef feeding lots with a sampling flow rate of 0.4 L/min for a couple of days [11]. So, in this research also, silicagel was used to adsorb volatile fatty acids. Charcoal is widely known for its capability to absorb broad range of volatile and non-polar compounds because of its high surface area.

Field Sampling

A dairy farm near Columbus, Ohio was selected as the CAFO facility for sampling odorous emission. Two field trips have been conducted on June 16 and Aug. 4, 2005 respectively. The weather condition on June 16 was cool and windy (Temperature from 60-75F), which resembles spring more than summer. Aug. 4 was a very hot day (Temperature around 92F) and can be representative of summer conditions. It is reasonable to assume the spring and fall conditions would be similar. We think winter sampling might not be necessary as the emission in winter can be low: the feeding barn and the milking house both have natural ventilation (heaters available), and the manure pond is frozen in winter with very little emission.

Samples were taken in the feeding barn, milking parlor and manure pond at the suggestion of the extension agent, which are considered representative for each type of odor. Average sampling period during field sampling was around 3.5 hours while the sampling flow rate was maintained at around 250 liters per minute. This sampling duration was determined to be safe as no breakthrough occurred during even 6 hour long lab sampling for validating the sampling system.

The feeding house is 108.8 ft by 195.6 ft. roofed facility with natural ventilation that has the capacity to accommodate approximately 800 cows. This facility is where cows are fed before being transferred every 6 hours to the milking parlor and being milked. The different activities associated with this facility are supplying feed, manure scraping, water spraying to cool off the cows during summer time, medical inspection of the cows and documentation, etc.

The milking house is 36 ft. by 80.6 ft. enclosed facility. This facility has two sections separated by an alley where workers can work. Each section can accommodate 25 cows. The cows are milked every 6 hours in this facility. Each milking cycle inside this facility lasts 5 to 7 minutes and the total time consumed in each cycle including the time taken to transfer the cows from the barn to the parlor may take up to 1 hour. Disinfectants were applied to the milking glands before and after milking.

The manure pond is where all the manure wastes from the feeding house are discharged through open channels. The pond is also divided into 2 sections by a partition wall. Each section or tank has the capacity to hold 54,000 lbs of manure discharge. The wastes from these two tanks finally get transferred to the third large tank from where the manure is taken out (pumped out) and applied in the crop fields. The level of the manure in the third tank was quite low as manure was recently applied in the crop filed for spring season.

The figures illustrated the sampling locations and a snapshot of each facility.

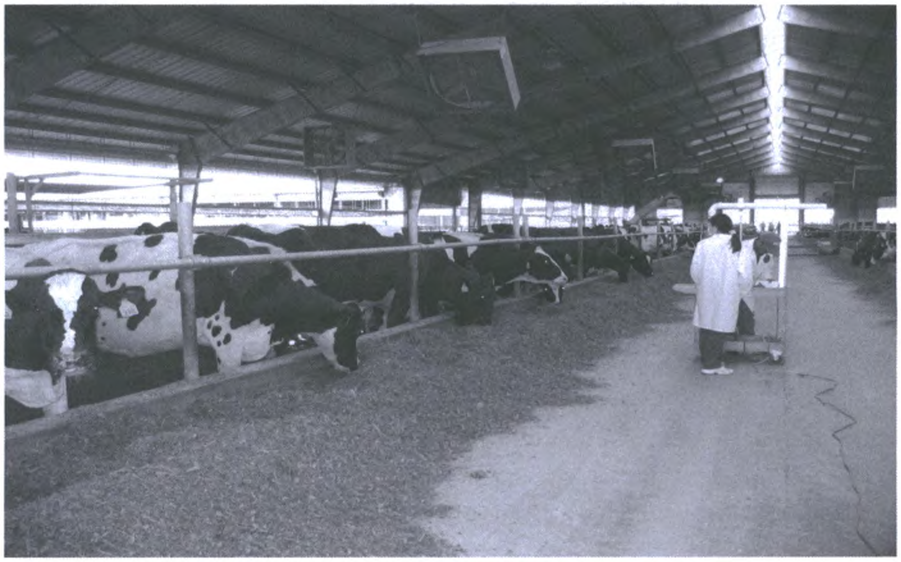

Figure 1: The Feeding Barn

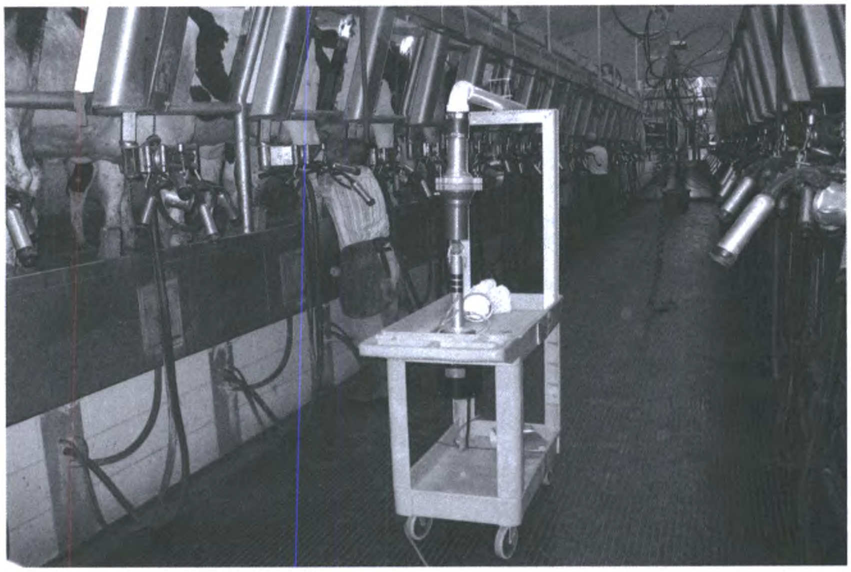

Figure 2: The Milking Parlor

Figure 3: The Manure Pond

Sample Extraction and Chromatographic Analysis

The samples in the sorbent cartridges were extracted separately using solvents. Each sorbent was first washed by methylene chloride (DCM) followed by methanol to further extract polar compounds. All of the wash liquids were concentrated by nitrogen evaporation to approximately 0.5-1.5ml, which were kept in sealable amber vials and stored in the refrigerator. The silica gel extract was derivatized with BSTFA (bis-trimethylsilyl) trifluoroacetamide) to analyze the volatile fatty acids (VFAs). The extraction and analytical methods were developed based on published results. The same extraction procedure was applied for the filter paper as well.

Compounds were obtained and mixed as described by Zahn et al. to make the synthetic swine odor. The synthetic swine odor was used in this research to validate the high volume sampling technique in laboratory, in addition, we also looked for the 19 compounds in the field samples.

Sorbent extraction is used rather than thermal desoprtion, the popular methods used in all the other studies. The primary reason is the size limitation of the thermal desoprtion unit, which only allows for 6-10mm tubes. The other drawback with thermal desorption technique is the high cost as the GC-MS system has to be dedicated to thermal desorption analyses only [12].

Results and Discussion

The chromatographic results from lab sampling proved that the customized sorbent assembly in overall was efficient in collection of the odorous compounds used in the preparation of synthetic swine odor solution. PUF was seen to be highly effective in absorbing non-polar compounds whereas silicagel was found to be more effective in absorbing volatile fatty acids. Charcoal and XAD were found to absorb similar compounds as PUF but in much lower quantities. Therefore, only the results from PUF and silica gel are reported. The laboratory sorbent validation is underway to further determine the optimized sorbent combination.

The results can broadly be classified in 2 major categories: quantitative and qualitative results.

The quantitative results were obtained from chemical standards, and are listed in Tables 1 and 2 for each field trip. It is noteworthy that out of these compounds, 4-Methyl phenol and 4-Ethyl phenol were the constituents in synthetic swine odor mixture solution which were seen in both first and second field PUF samples and were dominant peaks in case of second field sampling only. Other swine odor compounds seen in Feeding Barn PUF samples were Phenol, Methylindole and Indole.

The qualitative results were library search results based on the ten largest peaks obtained from GC-MS analysis. The dominant peaks seen in PUF extract for both first and second field sampling in case of the feeding barn were Hydromorphinol, Trimesitylborane, 4-Methyl Phenol, 4-Ethyl Phenol, Methoxy-phenyl oxime, 4-Octadecyl morpholine, etc.

Likewise in derivatized silicagel samples for the feeding barn, the dominant peaks include 1,2,3 trimethoxy 5-(2-propenyl) benzene; Hexanoic acid; Nonanoic acid; Octanoic acid tertbutyl dimethyl silyl ester; Decanoic acid, etc., out of which Hexanoic acid was the synthetic swine odor constituent that was dominant in both first and second field samples. Other swine odor compounds that were seen in Derivatized silica gel samples in both the field samples from Feeding barn even though were not dominant in peak size were: Valeric acid, Iso-Valeric acid and Benzyl Alcohol.

In case of Milking Parlor, the dominant peaks seen in PUF sample extracts for both the first and second field sample were for compounds such as : 4-Octadecyl Morpholine, 4-Methyl Phenol, 4-Ethyl Phenol, 3-Propyl Phenol, 1,3,5 trimethyl benzene, 2,4,6 tris (1,1 dimethylethyl) phenol, etc. Out of these compounds 4-Methyl Phenol and 4-Ethyl Phenol were the synthetic swine odor constituents. The other swine odor compounds seen in Milking Parlor PUF samples in both the field samples combined were Phenol and Benzyl alcohol.

Similarly, in case of derivatized silica gel samples for Milking Parlor for both the field samplings, the dominant peaks were found to be for compounds such as: Methoxyphenyl oxime, 4-Methyl Phenol, 4-Ethyl Phenol, Methandriol, Aphamethyl benzene methanol, and p-Xylene, etc. The Milking Parlor derivatized Silica gel samples were quite different from that of Feeding barn as no acidic compounds were seen as dominant peaks in this case which was anticipated for derivatized silica gel sample extracts. Moreover, the swine odor compounds that were seen in this case were also non-acidic compounds such as 4-Methyl Phenol and 4-Ethyl Phenol. No VFAs were seen in this sample.

The dominant peaks seen in case of PUF samples for Manure Pond in both the first and second field samples were for compounds such as Hydromorphinol, Trimesitlyborane, 4-Octadecyl morpholine, 4-Methyl Phenol, 4-Ethyl Phenol, 3-Propyl Phenol, Butylated Hydroxytoluene, etc. As in other PUF samples, 4-Methyl Phenol and 4-Ethyl Phenol were the synthetic swine odor compounds seen in this case as well. Other swine compounds seen but were not dominant were Phenol and Benzyl alcohol.

Similarly, the dominant peaks seen in derivatized silica gel sample for Manure Pond considering both the first and second field sampling were for the compounds such as: 2,5 bis [(trimethylsilyl)oxy] benzaldehyde; Benzoic acid 2-formyl 4,6 dimethoxy 8,8 dimethoxy oct - 2 - yl - ester, Silicic acid diethyl bis trimethyl silyl ester, Benzoic acid trimethylsilyl ester, Heptanoic acid, tertbutyldimethylsilyl ester, etc. No synthetic swine compounds were found among the larger peaks and hexanoic acid (trimethyl silyl ester was) the only swine odor compound seen in derivatized silica gel sample in second field sampling only for Manure Pond.

Out of those unidentified peaks, several of them may be nitrogen containing compounds. These are thought to be unique for diary operations, as they may come from the milk droplets or the disinfectant used. Further analysis of these compounds is necessary to identify and quantify them.

Table 1: Swine odor compounds seen in first field sampling

Site	**Feeding Barn**		**Milking Parlor**		**Manure Pond**	
Sorbent		**ppm**		**ppm**		**ppm**
PUF	4-Methyl Phenol	0.0022	Phenol	0.48	Phenol	0.23
	4-Ethyl Phenol	0.0024	Benzyl Alcohol	0.11	4-Methyl Phenol	9.09
	Methyl Indole	0.0024	4-Methyl Phenol	15.86	4-Ethyl Phenol	1.71
			4-Ethyl Phenol	4.58		
SG, Derivatized	Valeric acid	0.94	4-Methyl Phenol	0.0143	NONE	
	Iso-Valeric acid	0.54	4-Ethyl Phenol	0.0061		
	Hexanoic acid	1.07	Methyl Indole	0.0010		

Table 2: Swine odor compounds seen in second field sampling

Site	**Feeding Barn**		**Milking Parlor**		**Manure Pond**	
Sorbent		**ppm**		**ppm**		**ppm**
PUF	Phenol	0.62	4-Methyl Phenol	9.43	Phenol	1.79
	4-Methyl Phenol	29.70			Benzyl Alcohol	2.98
	4-Ethyl Phenol	7.94			4-Methyl Phenol	3.97
	Indole	0.19			4-Ethyl Phenol	1.64
SG, Derivatized	Benzyl Alcohol	0.025	NONE		Hexanoic acid	0.016
	Hexanoic acid	0.037				

Conclusion and Future Directions

The results of this preliminary study have indicated that the sampling system has been efficient in collecting the odorous emissions in the dairy farm. Sufficient mass has been collected within the 3 to 4 - hour sampling period. The selection of the sorbent materials and their assembly was suitable for diary farm application but further optimization of the sorbent is still needed. The effectiveness of solvent extraction needs to be further evaluated with the synthetic swine odor and compare with the thermal desorption method if possible.

The odorous compounds may be unique for each CAFO operation. Some of the compounds used in the synthetic swine odor mixture were not seen in the field samples, and there were some nitrogen containing compounds that are unique to dairy operations and need further identification.

More field sampling needs to be conducted to investigate the consistency and the reproducibility to evaluate the overall performance of the sampling system.

Acknowledgement

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Efficacy of Vegetative Environmental Buffers to Capture Emissions from Tunnel Ventilated Poultry Houses

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Introduction

Emissions of dust, gases and odors from poultry facilities pose major challenges for the poultry industry. In addition to environmental issues associated with air and water quality, nuisance complaints associated with alterations in the ventilations system and urban encroachment are becoming a greater concern. Cost-effective technologies to reduce these emissions from modern tunnel-ventilated poultry houses are limited. In late 1999 a University of Delaware-led initiative, in cooperation with the local poultry industry and various state agencies began an initiative of planting trees and shrubs around poultry farms. The goals of these vegetative environmental buffers (VEB) were to address environmental, neighbor-relations and production concerns (Figure 1). With support from US EPA, Region 3, Section 319 funds, a study was implemented to measure potential efficacy of VEB to capture emissions from a tunnel-ventilated poultry house.

Materials and Methods

In the Spring, 2002 a 30 foot wide, three row planting of 16 foot tall bald cypress (30 ft from fans), 14 foot tall Leyland cypress (40 ft from fans) and 8 foot tall Eastern red cedar (48 ft from fans) were installed directly opposite of two 48 inch tunnel cone fans on the northeast side of a house growing roaster chickens (Figure 2). Total depth (front to rear) of this planting was approximately 22 ft. Spacing between trees allowed the branches to touch, thus maximizing vegetative density. The goal of the planting design was to use the bald cypress as a pre-filter to catch large particulates and feathers, and to slow the air emitted from the fans. The Leyland cypress and Eastern red cedar provided maximum vegetative density to filter emissions. The reason for planting a deciduous tree on the inner row was to capture (and sometimes accumulate) large particulates during warm weather operation of the tunnel fans. These trees will then drop their leaves, with the attached particulates, in cold weather when tunnel fans are seldom operating.

Air quality monitoring stations were positioned 4 ft high opposite each of the two 48-inch diameter tunnel fans. Two stations were located directly in line with ventilation exhaust along the drip line in front of the tree barrier approximately 30 ft from the fan exhaust. The remaining two stations were positioned behind the VEB approximately 55 ft from the ventilation exhaust. During the fourth year of monitoring, sampling stations were positioned at both 4 and 8 ft high.

Air sample measurements included wind speed, total and respirable dust, ammonia and odor. General weather conditions (air temperature, wind speed and direction) were documented at the site during air sampling events. Data was collected during three-day periods prior to broiler movement (approximately 5-6 weeks of age) and again before roaster movement (7-8 weeks of age). To assure that sampling occurred only when tunnel fans were operating, all samples were collected from warm weather flocks during a five hour period from approximately 11:00 am to approximately 4:00 pm. Air sampling was conducted over four summers (2002-2005). To minimize the impact of crosswinds on the exhaust plume, a combination of temporary and permanent wing-walls were installed from the house to the edge of VEB during sampling events (Figure 3).

Total and respirable gravimetric dust concentrations were determined using NIOSH Methods 0500 and 0600, respectively. Flow rates of the pumps were calibrated at 2 L/min for measuring total dust concentration and 1.7 L/min for respirable dust concentrations. Pump flow rates were calibrated with a rotameter prior to and at the end of each sampling event. Sampling time averaged approximately five hours during tunnel fan operation. Both blank and background samples were obtained for each sampling event. The pre-weighed cassettes were supplied and analyzed by a certified laboratory (Data Chem Laboratories, Inc., Salt Lake City, UT). A Dust Trak Model 8520 (TSI Inc., St. Paul, MN) was used during 2004 as an additional procedure for total dust determination. These units provide the added advantage of getting real-time analysis during the 5-hour sampling events.

The primary method used to measure ammonia gas in this study was Gastec No. 3DL tubes (Gastec Corp., Ayase-City, Japan). Since ammonia concentrations exceeded the exposure limit of these 10 ppm tubes during our 5-hour sample period, multiple tubes were used during each sampling event. Sorbent tubes using NIOSH method S347 were also tried in 2002. Due to low ammonia concentrations in back of the VEB and the short 5-hour sample cycle, nearly one-half of the reported values were below the laboratory's (Galson Laboratory, East Syracuse, NY) detection limits. This method was discontinued. The impinger method OSHA ID -164 is a recognized procedure for ammonia determination. This method gave unexplained wide deviations in results and was also discontinued. It is important to stress that this study was a determination of the relative differences in emission concentrations between the front and rear of the VEB and consistency of results were most important.

For odor determination, an air sample was drawn into a 10 L Tedlar® bag at two locations; one in front and one behind the VEB. These samples were shipped overnight to The Iowa State Olfactometry and Air Quality Laboratory (Ames, IA) and were analyzed Within 24 hours after collection.

Results and Discussion

Over the past four years the growth (height) of the bald cypress, Leyland cypress and Eastern red cedar has increased 13, 24 and 25% per year, respectively. Dust and feather accumulation on the vegetation has been the greatest on the lower canopy of the Leyland cypress. This material continues to accumulate and is being retained over winter months, which may eventually affect health of these trees. To avoid this potential concern, a deciduous tree in the first row having greater density at the lower canopy, an alternative to the Leyland cypress that does not accumulate particulates and a greater planting distance from the fans, may be necessary. The current recommendation is to plant VEB at a minimum distance of 10 times the fan diameter (i.e. 4-foot diameter fan x 10 = 40 ft planting distance).

In this report the efficacy of VEB to abate emissions is expressed as the relative change (percentage) in concentrations from the front to the rear of this planting. Although potential dispersion losses across the width of the vegetation could not be measured with this experimental design, subsequent experiments suggest they are minimal. Because respirable dust concentrations were often below detection limits in the rear of the VEB these measurements were discontinued after the first year of the study. Based on 33 days of sampling over a four year period, the VEB reduced total dust by 49 ± 27% ($P<0.01$). Variation in efficacy of VEB to capture dust can be partially explained by wind direction during sampling events. Winds from the rear of VEB toward fans "*increased*" efficacy while opposite direction winds "*decreased*" efficacy. The wing-walls minimized the influence of crosswinds on measurement accuracy during sampling events. Background dust samples collected 300 ft away from the houses in a non-exhaust area were 94% less than concentrations entering the VEB. During 2004 both gravimetric and the Dust Trac determination procedures were used simultaneously during some sampling events and yielded similar results in relative efficacy; 35 vs. 39%, respectively. Air velocity from the fans was reduced 99% by the VEB.

Ammonia concentrations from 29 days of sampling suggest VEB reduced the concentrations by 46% ($P<0.01$). The standard deviation was +/- 31% and, again, can be partially explained by wind direction during sampling events. In 2005 both ammonia and dust reductions by VEB were greater at 8 ft compared to 4 ft height and may be explained by greater vegetative density in the higher canopy. Background ammonia concentrations were 93% less than samples obtained on the fan-side of the VEB. The fate of ammonia and nutrients in dust that accumulate on the vegetative filters is under investigation.

A more limited sampling of odor ($n=13$) found a non-significant reduction (6%) in odor concentrations and greater variability (standard deviation +/- 45%). Meteorological conditions and the type of crop next to VEB appeared to influence the efficacy of VEB to reduce odor. Wind direction appeared to have a greater influence on odor reduction by VEB than either dust or ammonia. Furthermore, when the field to the rear of VEB was in corn (crop within 4 ft) there may be a zone of stagnation coupled with wet, humid weather during some sampling events contributing to lack of efficacy of VEB to reduce odors. It is speculated that having openness behind these plantings may be a consideration to enhance VEB role in odor reduction.

Conclusions

The results and concept of using VEB as a cost-effective technology to abate emissions from modern tunnel ventilated poultry houses are encouraging. However, adoption of this practice by the Delmarva poultry industry has been driven primarily by its neighbor-relations benefits. The visual screen aspect of a VEB coupled with a proactive measure to address increasing urban encroachment issues are driving forces in acceptance of this technology.

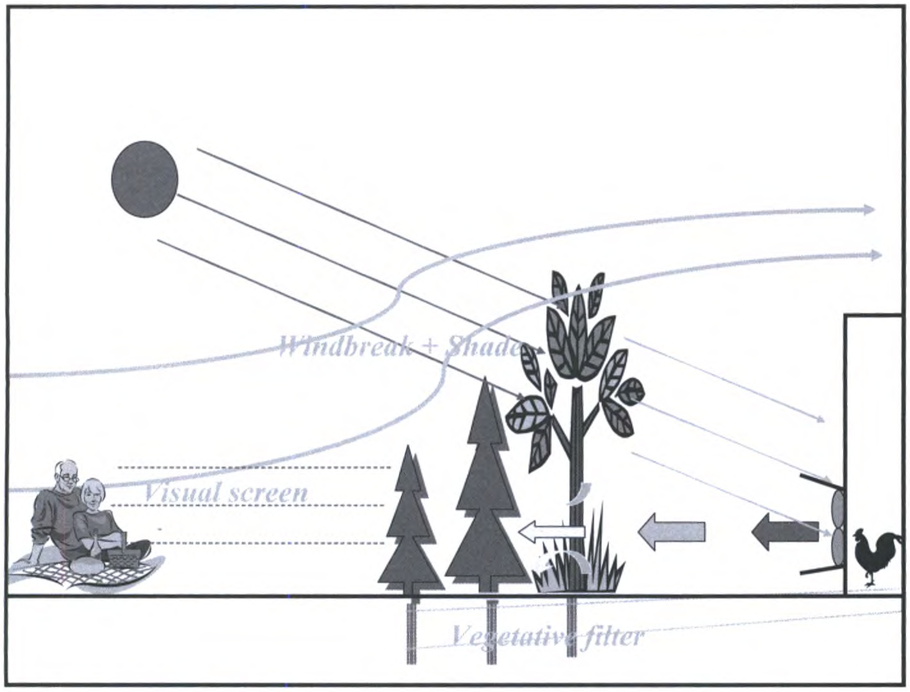

Figure 1. Goals of a vegetative environmental buffer.

Figure 2. Planting arrangement of trees opposite tunnel fans.

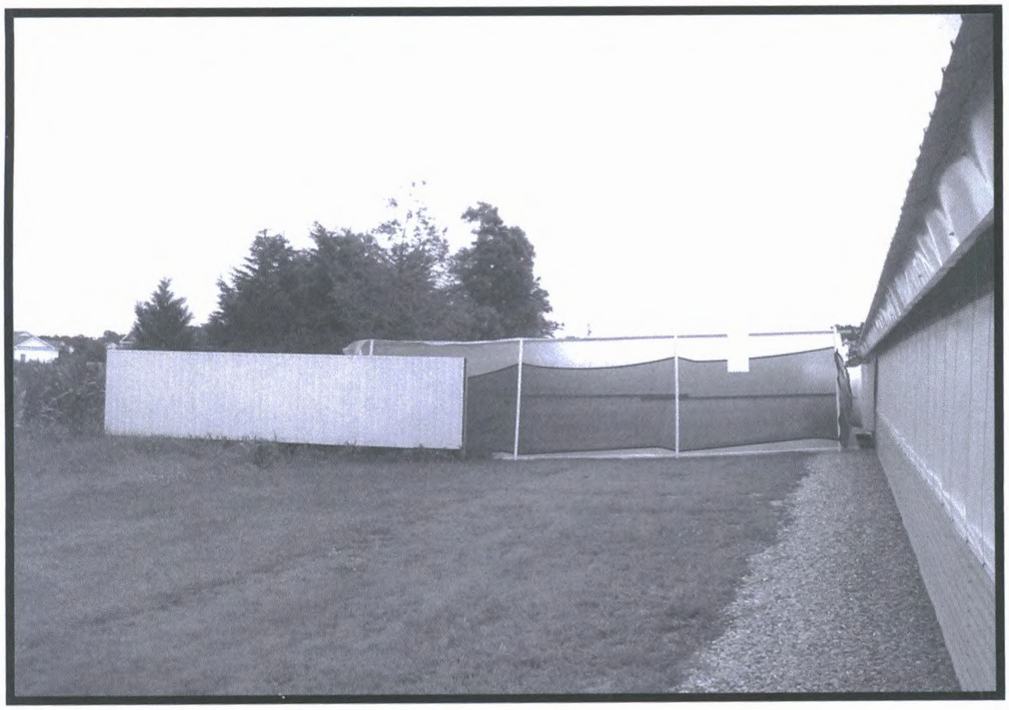

Figure 3. Wing-walls between fans and vegetative buffer installed to minimize influence of crosswinds on air quality measurements.

Establishment of Vegetative Environmental Buffers Around Poultry Farms

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Introduction

For many years the poultry industry has discouraged planting tall crops, shrubs or trees around poultry houses for fear the vegetation would restrict summer-time ventilation in naturally-ventilated poultry houses. However, in recent years the industry has shifted to tunnel-ventilated, windowless housing operations. Blocking airflow is no longer a major concern with this style housing. Emission of pollutants from poultry houses in general, and tunnel fans that are directed toward neighbors in particular, has become a major issue. These concerns have been compounded with urban encroachment around farms in many poultry producing regions of the country. Following several neighbor complaints about tunnel fans directed towards adjoining residual homes in the late 1990's, the University of Delaware started a proactive initiative of planting trees around farms as a visual screen, vegetative filter and shelterbelt/windbreak. Over the past five years 18 different demonstrations have been conducted to characterize various aspects in establishing vegetative environmental buffers (VEB) as a possible cost-effective strategy to address these urban encroachment and poultry-house emission issues. The following is a synopsis of these on-going efforts.

Lessons Learned From Vegetative Environmental Buffer Planting Demonstrations

The selection, arrangement and distance trees are planted from exhaust fans is critical. Observations to date suggest plantings be installed at a minimum distance of 10 times the fan diameter. Although evergreens with complex leaf shape are ideal for capturing particulates, plantings closer than 10 times the fan diameter sometimes results in severe feather matting and tree mortality. Planting deciduous trees in the first row closest to tunnel ventilation fans appears to be one option to avoid tree mortality. Particulates that accumulate on the vegetation during operation of these warm-weather fans drops-off with the leaves in the fall and the vegetative filter is renewed for the following spring. Evergreen trees with waxy leaves (i.e. holly), planted closer than 10 times the fan diameter in the first row opposite fans, appear to better withstand the high particular loads being emitted by the exhaust fans. Limited success was obtained with misting or washing off particulate loading on tree leaves. Although Eastern white pine plantings as the first row opposite fans have died apparently due to emissions, this tree may be an option in non-discharge areas. To address potential concerns of warm air from the exhaust fans causing thermal stress on the trees, temperature measurements in the exhaust plume were obtained from 36-inch sidewall and 48-inch tunnel ventilation fans during winter and summer, respectively. Compared to temperatures in non-fan plume areas, there does not appear to be any potential for thermal stress on trees at distances of 12, 22 and 42 feet from the fans.

Irrigation is essential to insure plant survivability, maximize early growth and is a requirement for growers receiving financial assistance for this practice in the region. Similarly, weed control is critical during the first few years of establishment of a VEB. An irrigation system using an emitter(s) to each tree and covering the row with weed mat or polyethylene appears to be an efficient way to address these matters. Recent hybrid willow cuttings planted in this fashion have achieved growths of 8 to 10 feet the first year.

Poultry growers that have implemented plantings incorrectly, failed to control weeds or provide irrigation have had marginal success in establishing a VEB. Therefore, poultry growers are strongly encouraged to seek technical assistance in the design, implementation and maintenance of VEB. The selection of plant material and arrangement of trees in a VEB plan must be designed for each side of every house, for each individual farm and must address the three goals of a VEB: visual screen, vegetative filter and shelterbelt. Retrofitting a VEB around existing houses poses many challenges due to boundary, structural, traffic patterns and other land-use restrictions. When the construction of new houses is being considered on the Delmarva Peninsula, the current recommendation is to include a VEB as part of the layout and design of the farm. To be responsive and proactive to escalating neighbor-relations and emission issues, the local poultry industry trade association plans to hire a coordinator to facilitate in the design, installation and maintenance of VEB on poultry farms in this area.

Air Emissions from Dairy CAFOs: Multi-scale Measurements and Process Based Modeling

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Introduction

Agricultural sources, especially livestock CAFOs, are being implicated more and more as major sources of atmospheric pollutants. Some of the major pollutants of concern tend to be ammonia, particulate matter (PM), methane, nitrous oxide, and carbon dioxide. Each has its specific concerns to public health and atmospheric degradation.

Emission of ammonia from animal agriculture has been heavily studied lately due to its large output from CAFO's and rapid reaction with strong atmospheric acids (nitric and sulfuric acid) to produce ammonium salts, also know as $PM_{2.5}$'s (Baek et al., 2004). $PM_{2.5}$ has been linked to reduced atmospheric visibility and negative health effects. In addition to its atmospheric reactions, ammonia can be dry deposited near its source contributing to soil acidification and decreased dissolved oxygen levels in streams and lakes. Due to its short lifetime (24 h to ~10d), it is generally regarded as a local problem, rather than a global one. The emission of ammonia is greatly effected by management techniques (Rotz, 2004), and season (Robarge et al., 2002).

Gases like methane, nitrous oxide and carbon dioxide are regarded as global problems due to their long lifetimes (>100yr), low volatility, and contribution to global warming. Methane sources from CAFO's have been well characterized for cattle, but other sources such as anaerobic lagoons, compost, and others are variable with season and management (Wuebbles and Hayhoe, 2002). The exact contribution of dairies to the emission of nitrous oxide is uncertain. It has been estimated that animal wastes and fertilizer account for about 8% of the global emissions (Godish, 2004), but other on farm practices are not estimated in the global budget. Methane, nitrous oxide, and carbon dioxide pose difficulties in modeling due to variations in management and ambient conditions (Miller and Berry, 2005), so direct measurement of there emissions is necessary for accurate estimates (Bouwman et al., 2000; Laubach and Kelliher, 2004).

This study aims at quantifying emissions of ammonia, ammonium, nitric acid, $PM_{2.5}$, methane, carbon dioxide, and nitrous oxide from multi-component dairy systems, and examining their spatial, diurnal, and seasonal variability. A parallel aim is to develop and challenge a process based model to estimate emissions.

The focus of the project is to provide accurate estimates of problematic trace gas and nitrogen emissions to the Colorado dairy industry, with the longer term goal to assist dairy producers in recognizing and mitigating environmental impacts.

Methods

System

Using a unique mobile sampling methodology employing 21 foot helium balloons and a variety of air and climatic sampling equipment, trace gases (carbon dioxide, methane, nitrous oxide) and N gas and particle species (nitric acid, ammonia, ammonium) were measured at five heights at three locations downwind, and three heights at one location upwind of two dairies. In addition, detailed micrometeorological data were collected for each sample height including temperature, relative humidity, wind speed and direction. These data were used to characterize the dispersion and concentration of the emission plume coming from the dairy. This innovative mass balance measurement technique was designed to overcome the limitations of other sampling systems and provide a spatially resolved characterization of the emission plume. For more detailed information about the measurement system, see accompanying conference paper entitled: **A** boundary layer sampling methodology for measuring gaseous emissions from CAFO's (Marcillac et al, 2006).

Emission Sampling Scheme and Site Descriptions

Measurements are currently being made at two Colorado dairies, seasonally, over two years from summer 2005 to spring 2007. To date, three of seven seasons (summer 05, fall 05, and winter 06) have been completed. The measurement plan calls for three measurement periods per day, conducted for two days, over 7 seasons at each dairy. Three daily sample periods allow us to analyze diurnal cycles and patterns in measured compounds.

The two dairies monitored have contrasting housing strategies, drylot (Dairy 1) vs. freestall (Dairy 2), but similar manure management systems (flush lanes, leaky dam and earthen pit solid separation, open lagoon storage, and composting). One distinct waste management difference between the two dairies is the composition of their lagoons. Dairy 1 has two waste lagoons (first is 6.1 acres, 10 ft deep; second is 13.6 acres, 20 feet deep), the first being a holding pond and the second being a flow over lagoon which has established a purple sulfur bacteria population. Effluent from the second lagoon is used as flush water for pen alleyways and is pumped on to crops lands seasonally. Dairy 2 has a single 10 foot deep, 8 acre lagoon, and is currently adding algae in an attempt to increase their dissolved oxygen levels. The lagoon effluent is used as flush water in the barns, and only sporadically applied to outside crop lands in response to limitations in evaporative losses. Additionally, Dairy 2 often times has a large crust layer on their lagoon, which has been shown to effect ammonia emissions (Misselbrook et al., 2005). Dairy 1 has no crust build-up.

Results and Discussion

Climatic Data

Climatic data for each sampling period are presented in Table 1. Data are shown for the morning and afternoon sampling periods to show diurnal variation. Additionally, each season is shown separately to illustrate seasonal differences. These factors are important when assessing the daily and seasonal emissions of the different gas and particle species. Most important for calculation of emission flux data is the wind speed and direction. The wind speed is used to estimate the spread of the plume, while the wind direction tells us where the plume is coming from. The integration of this information into an emission model is currently underway.

Emissions data

Preliminary results show that the concentration of each compound varies spatially with location downwind of the farm (Table 2) and height (Table 3), as well as seasonally (Table 2). To date, not enough data has been collected to show any significant diurnal variation in emissions.

Upwind vs. Downwind. The upwind data should mimic global background for trace gases, and local background for volatile N species (Table 2). Unfortunately, local backgrounds of nitric acid, ammonia and ammonium were not known, so we consider our upwind values as the local background concentration. Our upwind concentrations were slightly higher than global backgrounds, indicating significant additions from local sources.

Table 1. Summary of seasonal climatic data for each experimental Colorado dairy

Measure	Date	Press mb	Temp °C	RH %	Wind Speed mps	Wind Dir deg
Dairy 1						
Summer, morning[a]	07/19/05	851	26.8	26.7	2.4	214
Summer, afternoon[b]		851	26.6	27.0	2.4	226
Fall, morning	NA	-	-	-	-	-
Fall, afternoon		-	-	-	-	-
Winter, morning	01/26/06	847	3.8	31.6	1.0	177
Winter, afternoon		844	9.2	17.9	3.2	184
Dairy 2						
Summer, morning	07/28/05	832	23.2	30.5	2.3	194
Summer, afternoon		841	30.9	18.1	4.3	157
Fall, morning	11/18/05	842	8.1	26.9	3.3	149
Fall, afternoon		839	11.3	21.1	2.0	156
Winter, morning	01/30/06	834	3.8	22.0	2.2	168
Winter, afternoon		833	7.0	20.4	3.4	180
Seasonal Averages						
Summer	July	844	26.9	25.6	2.8	198
Fall	November	840	9.7	24.0	2.7	152
Winter	January	840	5.9	23.0	2.4	178

[a] Morning is any sample time before 1100 h

[b] Afternoon is any sample time between 1100 - 1700 h

Trends. Trends in some of the gases have been seen. Nitric acid tends to have a higher upwind concentration indicating that some of it is consumed as it passes through the dairy. Given the high ammonia concentrations found at the dairies, we speculate that nitric acid and ammonia are reacting at the dairy to form ammonium nitrate. This is supported by increases in total ammonium levels in downwind concentrations. The relatively small increases of ammonium species may be the result of the close sampling proximity to the dairy (less than 200 m). We surmise that ammonia doesn't have sufficient time to react with H^+ ions (nitric acid, sulfuric acid, water, etc.) to create ammonium compounds, in this situation.

Seasonal. Seasonal variation was seen for each species. So far only three seasons (summer, fall and winter) have been analyzed for trace gases and two seasons (summer and fall) for N species. On average, we have found that nitric acid and ammonium levels increase with colder seasons (fall and winter), and ammonia increases with warmer seasons (summer). This trend follows expected species behaviors for changes in temperature. Trace gases were all highest in summer, and lowest in fall. Fall and winter concentrations did not differ greatly, but this could be because average seasonal temperatures were close to each other (within 4° C).

Table 2. Summary of gas and particle concentrations by location and season

Measure	HNO3 ppbv	NH3 ppbv	NH4 ppb(w/w)	CO2 ppmv	CH4 ppmv	N2O ppbv
Global background[a]	*NA*	*1-10*	*NA*	*370*	*1.72*	*320*
Total upwind, avg	1.89	48.8	0.37	399	2.01	326
Total downwind, avg	1.64	236.1	0.45	406	2.34	328
Seasonal downwind, avg						
Summer	1.00	299.5	0.36	420	2.49	329
Fall	2.93	109.3	0.63	396	2.13	326
Winter	-	-	-	397	2.29	327
Spring - No data yet	-	-	-	-	-	-

[a] Data from Godish, 2004

Vertical profile. Peak concentrations for all compounds, except nitric acid, were found at or near ground level, reflecting a strong local source (Table 3). Nitric acid peak concentrations were at higher elevations, indicative of its more remote source. Ammonia had a clear vertical profile, with a max concentration at the lowest sample height (2m), and decreasing steadily with height. Most other compounds did not show a clear pattern, but rather had multiple peaks, usually at the bottom, middle, and top heights. Further data collection is needed to verify if this is a trend or not.

Table 3. Summary of gas and particle concentration by sample height

Measure	HNO_3 ppbv	NH_3 ppbv	NH_4 ppb(w/w)	CO_2 ppmv	CH_4 ppmv	N_2O ppbv
Total downwind, avg						
Height 1 (Top)[a]	1.60	39.1	0.37	404	2.28	327
Height 2	1.92	124.9	0.46	401	2.23	327
Height 3	1.65	246.9	0.47	405	2.35	327
Height 4	1.42	357.4	0.44	406	2.35	328
Height 5 (Bottom)[a]	1.63	426.9	0.52	414	2.47	329

[a] Measurement height varied with each data collection period based on climatic data. The top height is the highest collection height, and the bottom height, the lowest collection height.

Diurnal. No clear diurnal pattern has yet been verified. Additional data and seasonal replication will need to be collected to identify any diurnal patterns.

Future Work

The goal of the project is to develop and test process based estimations of CAFO air emissions. First, the species, climatic, and spatial data will be integrated into a model that will attempt to show the behavior of the emission plume. Additionally, a model will be created to characterize ammonia emissions by estimating ammonia fluxes from specific farm components and validating those values with data collected by the system.

The multi-scale measurements and modeling associated with this project will investigate emissions outputs along with diurnal and seasonal variability.

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A Boundary Layer Sampling Methodology for Measuring Gaseous Emissions from CAFOs

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Introduction

Confined animal feeding operations (CAFO's) are known to be major contributors of atmospheric gaseous and particulate pollutants, but the magnitude and timing of these emissions is poorly known. Various methodologies have been employed to measure CAFO emissions (e.g. flux chambers, lasers, and stationary towers), but these methods are usually limited in their ability to fully characterize the emission plume from a heterogeneous farm, and thus are limited in their ability to quantify total emissions. We present a whole farm measurement system that overcomes these limitations by sampling concentration and wind speed profiles to characterize the horizontal and vertical extent of the plume at relatively high temporal resolution (30-120 min).

The system is designed to measure trace gases (carbon dioxide, methane, and nitrous oxide) using syringe pumps, and N species (nitric acid, ammonia, and ammonium) using specially designed filter packs. The validity of the gas and particle samples obtained by our system needed to be assessed by testing the method and set-up used for recovery of the atmospheric gases. For the trace gas sampling, we conducted a field test using methane gas as a recovery gas. The filter packs, used for N recovery, were tested in the lab for recovery potential, then field validated with URG denuder samplers.

The objective of the study was to demonstrate the validity of the system in the lab and field conditions, as well as test the precision of the sampling equipment in the field.

Methods

Set up

Our unique method employs four 21 foot mobile tethered helium balloons (Blimp Works, Statesville, NC), three spaced downwind across the farm perimeter and one upwind. Gas and particulate sampling systems are attached to the tether lines at five heights. Sample heights and tether locations varied depending on wind direction and anticipated plume height estimated using a Gaussian plume model. Trace gas and particulates were collected using impactor and filter systems attached at each height, with less reactive gases pumped to the ground and collected using syringe pumps. The filter packs, specially designed for this system, collect PM, ammonium, nitric acid, and ammonia, while the syringe pumps collect methane, carbon dioxide, and nitrous oxide. Detailed climatic data (wind speed, wind direction, temperature, relative humidity, and pressure) are measured at the five sample heights using a DigiCORA Tethersonde System (Vaisala, Boulder, CO). Average wind speeds, taken at each height along with mean gas and particulate concentrations, are used to estimate mean vertical and horizontal flux at each sample location and be integrated with respect to location to estimate mass flow within the plume.

Validation

Filter packs. The filter packs used for sampling were modified Teflon URG 25 mm Filter Pack Samplers (URG, Chapel Hill, NC), designed for a flow rate of 4 lpm. Originally designed to hold just one filter, we modified the inside of the sampler to hold three filters in an aluminum cartridge. The stainless steel cartridge set inside the bored out filter pack, and inside of it were three filters, each separated by a Teflon o-ring and a Teflon coated stainless steel screen. Three different 25 mm filter types were used for sampling:

Teflon (PM and ammonium), nylon (nitric acid), and quartz (ammonia). At the top of the filter pack, near the inlet was an impaction plate that had a particle size cutoff of 2.5 µm at a flow of 4 lpm. While the filter pack inlet was left open to sample ambient air, the outlet was connected with Teflon tubing to a filter pump which pulled air through the filter pack at a rate of 4 lpm. The pump was regulated by a rotometer, calibrated before each use.

Filter packs were tested in the laboratory for system leakage and ammonia recovery efficiency. They were also lab and field tested side-by-side for accuracy of collection against a URG denuder system for nitric acid, ammonia, and sulfate recovery. The URG denuder system is considered a valid system for gas recovery.

Extracts from all the filters and denuders were analyzed by ion chromatography (IC) on a Dionex Model DX500 IC using standard techniques of ion chromatography.

System. In order to test the validity of the entire measurement system, and its gas recovery ability, the system was set up in an open field and tested with tracer of pure methane gas. The field test brought into play the various climatic conditions we would face such as wind speed and direction, temperature, and relative humidity. All of these factors affect the rate of gas recovery; it was our goal to see how much.

Field experiments were carried out in an open, clean-air location with no surrounding animal operations or known methane sources near by. An experimental methane plume was created by releasing pure (99.97%) CP grade methane gas at constant flow rates from three 200 ft^3 (5,663 L) cylinders situated 50 m from each other and orthogonal to mean wind direction. The tanks were located at ground level and gas was routed through a perforated tube extending 5 m from the tank. This was an attempt to recreate a surface emission scenario, as would be seen on a dairy farm. The tethered balloon sampling system was set up with the four balloons, one upwind and three downwind. The balloons were spaced 100 m from each other, and 200 m from the methane source. They were deployed to measure upwind (background) and downwind (plume) concentrations, with sample heights at 40, 20, 10, 5, and 2 m above ground level. The heights were calculated based on current climatic conditions using a Gaussian plume model which predicts plume height based on distance and wind speed parameters. In theory, the top height was located just at or above the top of the plume. The tethersondes were attached at each sample height and recorded climatic data for each sample period (Table 1).

Methane was released into the air at a controlled rate of 70 lpm, and air samples were collected in 30 min intervals with a five minute acclimation period prior to sampling. Sample times were at 1410, 1517, and 1612 h. A 25 min dispersion period was allocated between sample periods to allow the methane gas from the previous sampling to disperse.

After collection, samples were injected equally into two evacuated vials for later CH_4 analysis by GCMS.

Results and Discussion

Climatic data. Climatic data were logged for each sample period (Table 1). Climatic data were used for calculation of methane dispersion and recovery rates. The wind direction data for each period was relatively stable, with only slight shifts in ranges. For period 1, the wind direction was between 180 – 247°, 86% of the sample time, and 202 – 225°, 56 % of the sample time. Period 2 had a majority of spread between 157.5 – 202.5° (80.3%), and 157.5 - 180° for 60.5 % of sample time. Period 3 had an average of 135 – 180°, 80% of sample time, and 157.5 – 180°, for 68% of sample time. This showed that the wind direction was stable within 23° for 60% the sample time, but that the methane plume was not always in line with the samplers for the rest of the time. We could expect slightly lower or higher recovery values than predicted at each location based on this data. Additionally, based on the wind speed and spread of the plume, some of the sample locations might have different values than others based on overlap of plumes.

Table 1. Climatic data summary for each sample period

Measure	Press mb	Temp °C	RH %	Wind Speed mps	Wind Dir deg
Period 1	851.25	8.57	34.85	3.18	202.14
Period 2	850.57	9.83	30.97	3.47	165.62
Period 3	850.28	10.53	29.16	3.23	154.25
Total	850.70	9.64	31.66	3.30	175.41

Filter pack. Lab tests showed that the filter packs had virtually no leakage around the modified filter apparatus (Table 2). For generated ammonia, lab tests showed that the filter packs had a 97% ammonia collection efficiency. When compared against the denuder sampler, the two systems had variable recovery rates for each species in the field. Some of this variation is due to slightly different locations of the samplers in the downwind plume, as well as handling errors. On average we assume a 5% error when comparing the two systems.

Table 2. . Summary of filter pack performance

Measure	Collection, %
Leak test effiency, %	97.5
Ammonia recovery, %	97.7
	Differentiation, %
Comparison of filter pack and denuder, %	
Nitric acid	21.9
Ammonia	16.7
Ammonium	4.4

System. Results of the field methane recovery are listed in Table 4. The release rates were calculated for each sample period based on gravimetric analysis. The expected recovery rates were calculated using a Gaussian plume distribution equation based on release rate and climatic data collected during the sampling period (Table 3). The equation predicts the steady-state concentration of methane at a point (sampling inlet) located downwind of the emission source, which in this case are the methane bottles.

The methane concentrations measured downwind were less than the expected recovery rates for each sample period (Table 3), but some deviation was expected based on the wind direction patterns. For sample period 3, we see a 96% collection efficiency. Upon analysis of the wind direction data, we find that the winds were in direct line (less than a 20º variation in wind direction) with the samplers for over 80% of the sample time, allowing for a good recovery. For sample period 1, we see only a 16% recovery of methane. This is because the winds were only in direct line with the samplers for 7% of the sample time. Sample period 2 had good wind alignment for 40% of the sample time, which also corresponds to the recovery efficiency. This shows how important consistent wind direction is for accurate sample obtainment of a point source emission when using this system. Any variation over a 40º wind direction shift will remove the emission source from the sample stream. When sampling on a dairy, the entire plume is taken into consideration, so this effect has a reduced input, since interest is on the entire emission form the dairy, not just a single source.

Table 3. Calculated release rate, expected and actual recovery rates of released methane gas

	Sample Period		
Measure	**1**	**2**	**3**
Release rate, g/sec	2.42	1.99	1.94
Expected recovery[a], ppm	0.18	0.14	0.15
Actual recovery, ppm	0.03	0.06	0.14
Recovery rate, %	16	43	96

[a]Based on Gaussian plume calculations for ambient conditions

Table 4. Summary of methane recovery data

Measure	**Mean**	**STD**	**Min**	**Max**
Average background (upwind), ppm	1.92	0.02	1.87	1.93
Average downwind[a] conc, ppm	0.07	0.07	0.01	0.29
Total concentrations by location, ppm				
Downwind 1	0.10	0.10	0.02	0.29
Downwind 2 (center)	0.08	0.05	0.01	0.15
Downwind 3	0.04	0.02	0.01	0.07
Total concentrations by height, ppm				
Height 1 - 40 m	0.09	0.07	0.01	0.21
Height 2 - 20 m	0.08	0.05	0.04	0.17
Height 3 - 10 m	0.09	0.11	0.01	0.29
Height 4 - 5 m	0.05	0.05	0.01	0.11
Height 5 - 2 m	0.06	0.08	0.02	0.23

[a]Downwind is the total downwind concentration minus the background (upwind) methane levels.

Conclusion

The air sampling methodology outlined here has been validated as an effective means of collecting N species (nitric acid, ammonia, and ammonium) with filter packs, as well as trace gases (methane, carbon dioxide, nitrous oxide) with syringe pumps. The use of weather monitoring equipment (tethersondes used here), is vital to the validity of this data, as the wind speed dictates the spread of the plume, the wind direction the collection efficiency, and the temperature, pressure and RH the concentration of the gas or particle species. We have illustrated that the wind direction can pose difficulties in the collection of data, as any shift will change the collection concentration of the gas species. We have made our samplers mobile in order to adjust for this dilemma, but sample times must be compromised if a change in location is necessary. The mobility of the system makes it easy to use over the course of the day by maintaining a downwind location. Additionally, this method gives the concentration of species at five different heights, showing the different vertical profiles. This could prove to be a very valuable tool in selecting monitoring heights of different gas and particle species.

Determination of Particle (PM_{10} and $PM_{2.5}$) and Gas-Phase Ammonia (NH_3) Emissions from a Deep-Pit Swine Operation using Arrayed Field Measurements and Inverse Gaussian Plume Modeling

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Abstract

The contribution of agricultural emissions of primary (direct) and secondary (precursor) pollutants to air quality is rapidly being recognized as an important fraction of local and regional air pollution budgets. However, a significant uncertainty still exists in the magnitude and rate of these types of emissions, especially under "in field" conditions common within the central and western United States. Described herein are the results of a study conducted at a deep-pit swine production facility in central Iowa. The facility consisted of three separate, parallel barns, each housing around 1,250 pigs with an average weight of approximately 90 pounds per animal. The area around the facility was topographically flat and surrounded by soybean and cornfields. A number of portable $PM_{10}/PM_{2.5}$ (AirMetrics MiniVol) samplers and passive NH_3 (Ogawa Model 3300) samplers were arrayed vertically and horizontally around the three-barn production facility, and data were collected on a daily-averaged basis for approximately three weeks in August and September of 2005. Additionally, a monitoring station was established approximately 40 m to the north of the nearest barn to record the typical suite of meteorological parameters (wind speed, direction, temperature, etc.) for determination of near-source atmospheric advection and dispersion. The AirMetrics samplers were operated with $PM_{2.5}$ impactor separation heads for approximately the first half of the field study and were then switched to the PM_{10} heads for the remaining portion of the study. Each AirMetrics sampler was fitted with a conditioned, preweighed Teflon filter and operated at approximately five liters per minute for a time-controlled 23-hour period. Following sampling, the filters were recovered, conditioned, and reweighed at USU's Utah Water Research Laboratory (UWRL) in Logan, UT for filter catch and ultimate determination of each location's $PM_{2.5}/PM_{10}$ mass concentration. The Ogawa passive samplers were co-located and operated for the same time periods with the pre-treated (acid-coated) collection pads recovered after the same 23-hr period and stored appropriately until the final analysis for NH_3 concentrations could be performed via ion chromatography at the UWRL facility. Emission estimates were derived via the comparisons of the measured particulate and NH_3 concentrations at each sampling location with the concentrations for each receptor (sample) point found via application of the EPA-recommended ISCST3 air dispersion model (Lakes Environmental Software). The comparison of the measured and model predicted NH_3 concentrations resulted in a derived NH_3 emission rate of 17.22 ± 7.2 g/pig/day. This value is slightly more than two times greater than referenced emission rates; however, the two emission rates are within statistical uncertainty of each other. The analyses for the particulate emissions are as yet incomplete; however, preliminary calculations show PM_{10} and $PM_{2.5}$ emission rates of 0.55 and 0.14 g/pig/day, respectively.

Introduction

The existence of fine particulate matter in the atmosphere is the result of a complex combination of direct source (primary) emissions and photochemical (secondary) formation reactions. In broad terms, the composition of fine particulate, typically defined as $PM_{2.5}$ or suspended particulate matter with a diameter of less than 2.5 μm, is often broken into five basic categories: (1) crustal elements, (2) organic carbon, (3) elemental carbon, (4) ammonium sulfate, and (5) ammonium nitrate (Malm, 2000). The significance of any particular compositional element is often a strong function of locally dominant source categories.

The contribution of agricultural emissions of primary (direct) and secondary (precursor, especially ammonia) pollutants to air quality has only recently been recognized as an important fraction of local and regional air pollution budgets (Bicudo et al., 2002). However, a significant uncertainty still exists in the magnitude and rate of these types of emissions, especially under "in field" conditions common within the central and western United States (CENR, 2000; FAO, 2001; CAEAFO, 2002). As such several local and regional agricultural emission projects have been reported over the last few years (Hoff et al., 2005; Heber et al., 2005; and others).

As a part of a larger field investigation (Bingham et al., 2006; Zavyalov et al., 2006; and others), studies described herein were conducted at a swine finishing facility near Ames, Iowa to examine the facility-wide emissions of PM_{10} and $PM_{2.5}$ and gas-phase ammonia (NH_3) using arrayed field measurements of the target species, followed by subsequent inverse modeling using an EPA-approved Gaussian dispersion model.

Methodology

The field measurements took place from August 24 to September 7, 2005. A three-barn, deep-pit swine finishing operation located near Ames, Iowa was the site selected for the study. Each barn housed approximately 1,250 pigs, with an average weight during the test period of 90 pounds. The barns were 21.8 m apart, all aligned in a parallel east-west orientation, with each barn being 12.6 m wide and 79.5 m long. A 1.4 m tall screen-vented window ran long the north and south sides of the barns. These windows were equipped with retractable canvas shades, but these were rarely employed throughout the duration of the test.

Based on historical meteorological data, portable $PM_{2.5}/PM_{10}$ and NH_3 samplers were deployed in a generally north-south array in and around the facility. Most of the samplers were deployed on tripod supports at a height of about 2 m above ground level (see Figure 1). Additionally, elevated samplers were placed on a meteorological tower between two of the barns and on a second tower in a cornfield to the north of the facility.

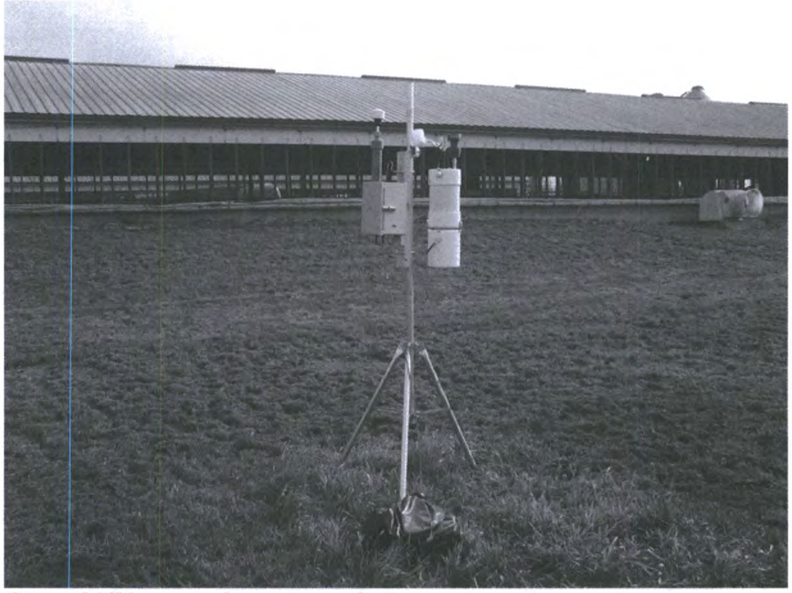

Figure 1. Particle and NH_3 samplers near pig barn

The particle samplers used were AirMetrics MiniVol $PM_{2.5}/PM_{10}$ samplers. These samplers are self-contained (particle collection mechanism, pump/flow control, and battery) and can be programmed to operate for any desired time period. The MiniVols separate for PM_{10} or $PM_{2.5}$ depending on which fractionation head is installed on the unit. The particulate matter was collected on pre-weighed Teflon filters, which were transported back to Utah State University (USU) for final weight determination and concentration determination. From August 24 to September 1, the systems were configured to sample for $PM_{2.5}$; during the remaining test periods the samplers were configured for PM_{10}.

Ambient ammonia concentrations were monitored via passive sampling monitors described by Roadman et al. (2003). The samplers consist of a citric acid-treated quartz fiber pad, a series of diffusion screens, an inert housing, and a rain shield. The samplers were exposed at the arrayed locations for a recorded period of time and recovered into air-tight containers. The pads were then transferred to individual sampling bottles until they could be returned to USU for NH_3 analysis using ion chromatography.

The sample collection periods were broken into 23-24 periods for each system. In addition to the pollutant measurements ,on-site meteorological data were also collected. Emission points (barns) and sampler locations were all recorded using a hand-held GPS system.

The pollutant concentrations, source/receptor locations and meteorology were used in conjunction with the U.S. EPA's Industrial Source Complex, Short Term (ISCST3) Gaussian plume dispersion model to back calculate the emissions required to observe the monitored pollutant concentrations. The specific software used was the ISC-AERMOD package marketed by Lakes Environmental Software. In brief, the model was operated for the chosen time period, using observed meteorology and a "seed" value for the initial emission rates. After several approaches it was determined that treating the barns as volume sources most reliably produced results similar to the observed concentrations. The initial emission rates were obtained from those reported by other investigators for similar facilities (Hoff et al.; 2005). The initial NH_3 emission rate was assumed to be 7.43 g/pig/day, while the initial PM_{10} and $PM_{2.5}$ emissions were assumed to be 0.11 g/pig/day and 0.028 g/pig/day (since no separate value was given for $PM_{2.5}$, its emission rate was assumed to be 25% of the PM_{10} rate). Modeled concentrations at the specified receptor (sampler) locations were then compared to the observed values. The ratio of the observed values to the modeled values were then compiled and used as a multiplier for the "seed" emission rate to derive the on-site specific value.

Results and Discussion

The observed ammonia concentrations ranged from 6.8 $\mu g/m^3$ farthest or upwind from the barns to 905 $\mu g/m^3$ nearest the barns. Samplers that were determined to be upwind or completely crosswind from the source, and therefore not affected by barn-generated emissions, were treated as local/regional background samples and subtracted from the barn-impacted samples. The average NH_3 background sample was found to be around 25.7 $\mu g/m^3$. The elevated locations (met towers) generally showed lower concentrations than samplers posted on the same towers but at lower elevations.

Overall, the modeled NH_3 concentrations were on the same order as the observed values, with a few notable exceptions. The model was unable to adequately account for plume buoyancy and nearly always under-predicted the concentrations at the elevated receptor locations. Furthermore, the concentrations predicted by ISCST3 for the upwind or crosswind areas were usually zero or much less than $1 \mu g/m^3$, which also led to much smaller values than observed for those receptors.

The under prediction of the modeled concentrations for the extreme receptor locations resulted in anomalously large concentration ratios (measured over modeled) for these fringe sites (see Figure 2). If all of the receptor/sample locations are included, the overall average NH_3 concentration ratio was found to be 44.0 ± 52.6 (the uncertainty represents the 95% confidence interval). This would mean that the derived emission rate would need to be 44 times the assumed "seed" emission rate of 7.43 g/pig/day.

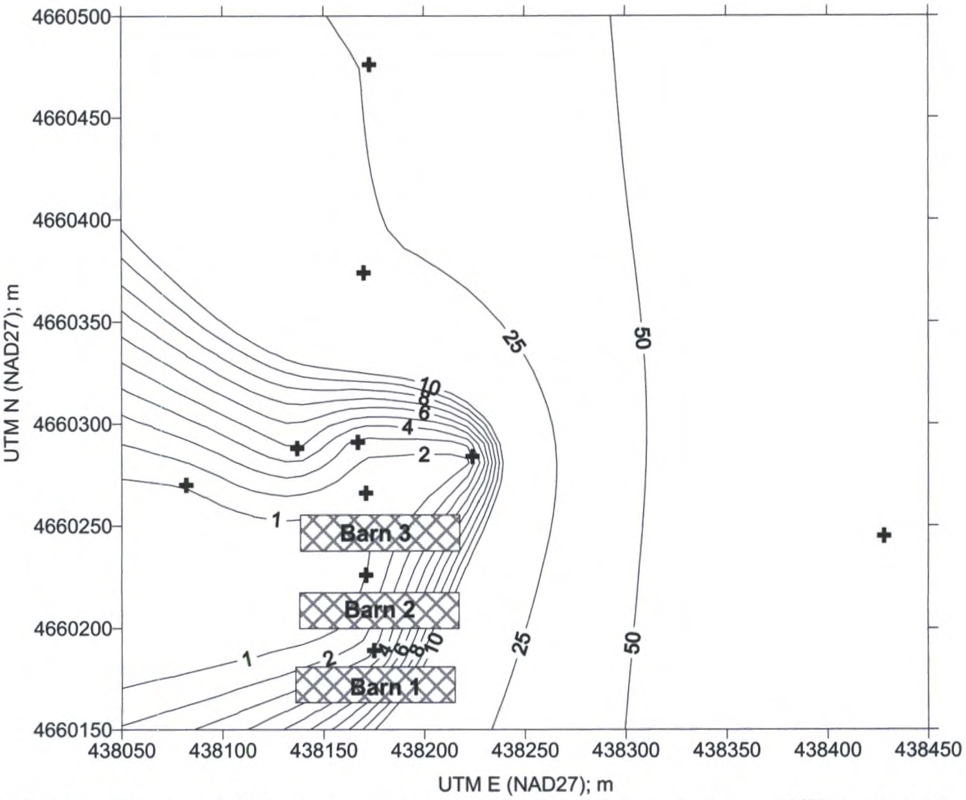

Figure 2. Isoplethic map of the overall averaged ratio of the observed NH_3 concentrations to the modeled NH_3 concentrations.

A more realistic NH_3 emission rate can be derived, however, if the elevated and non-plume receptor points are ignored. By discounting the under-predicted locations, essentially all points outside of the "6" isopleth in Figure 2, the average concentration ratio (measured to predicted) becomes 2.32 ± 0.96, which equates to an average emission rate of 17.2 ± 7.2 g/pig/day. This value is higher than, but statistically indistinguishable from, that of Hoff et al. (2005).

The data for the particulate measurements and modeling are, as of this writing, still incomplete. However, preliminary analysis suggests that arrayed, mass-based field measurements may not be the best way to quantify particulate emissions from this specified type of agricultural facility. Background, non-barn influenced PM_{10} and $PM_{2.5}$ concentrations were found to average around 35 and 10 $\mu g/m^3$, respectively, while in-plume values were 40-60 and 10-15 $\mu g/m^3$, respectively, depending on sampler location relative to the barns. This suggests approximately 15 $\mu g/m^3$ of the nearby atmospheric PM_{10} may be attributable to the swine houses. Similarly, up to 5 $\mu g/m^3$ of the local $PM_{2.5}$ may be attributable to the examined sources.

ISCST3, using Hoff et al.'s (2005) PM_{10} emission rate of 0.11 g/pig/day, predicted barn-induced PM_{10} contributions in the range of 0.62-3.48 $\mu g/m^3$, depending on the receptor location. Scaling the emission rate for $PM_{2.5}$ results in expected fine particle concentrations in the range of 0.02-0.81 $\mu g/m^3$. These numbers suggest the model-derived particulate emission rates are greater than five times the initial "seed" values. This would give PM_{10} and $PM_{2.5}$ emission rates of 0.55 and 0.14 g/pig/day, respectively.

Conclusions

The approach of coupling field-arrayed concentration measurements and inverse Gaussian modeling proved to be a valid and reasonable approach for modeling gas-phase ammonia emissions from the examined three-barn, deep-pit swine finishing facility (3,750 total animals). The derived NH_3 emission rate of 17.22 ± 7.2 g/pig/day was slightly more than a factor of two greater than the referenced emission rate (Hoff et al., 2005), but within the range of statistical uncertainty.

Owing to the expected low emission rates of the particulate matter, the observed differences between the local/regional background PM_{10} and $PM_{2.5}$ made determination of robust emission rates difficult. However, the ISCST3 model did demonstrate that the three swine barns were not an overly strong source of ambient particle. Preliminary analysis estimated PM_{10} emissions of 0.55g/pig/day and $PM_{2.5}$ emissions of 0.14 g/pig/day. Due to the limitations discussed previously no statistical uncertainties can be calculated at this time.

For facility-wide particle emissions, when the facility cannot easily be enclosed or otherwise encapsulated for direct flux measurements, techniques other than mass-based methodologies may need to be examined. These may include LIDAR systems or field-arrayed measurements similar to those described herein, but would need to utilize particle counters as opposed to filter collection.

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Morphology of Sulfate-Nitrate-Ammonium-Proton Aerosol Particles at Low Relative Humidity

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Abstract

Aerosol particles play a critical role in the chemistry of the atmosphere by providing surfaces for heterogeneous reactions and by serving as sinks and sources of atmospheric gases. Sulfate-nitrate-ammonium-proton (SNA) particles are particularly important because they make the largest anthropogenic contribution to the aerosol mass budget on a global basis. The ammonium content, which regulates acidity, originates almost entirely from agricultural activities. In the current study, the morphology of SNA particles having aqueous and crystalline components after exposure to low relative humidity is studied. We find that the morphology of internally mixed aqueous and crystalline particles depends on chemical composition as well as specific history of relative humidity. Current data suggest that compositions containing nitrate have a morphology with a crystalline core and an aqueous layer, while compositions that do not contain nitrate crystallize with enclosed pockets of aqueous solution. The rate at which relative humidity is decreased also seems to affect the formation of enclosed pockets. Knowledge of the morphology of SNA particles increases our understanding of how particles interact with the surrounding gas phase and can be used to better predict reaction rates in atmospheric chemical transport models.

A Global Modeling Study of Aqueous or Crystalline Ammonium and Sulfate Particles in the Troposphere

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Abstract

The physical state of tropospheric ammonium and sulfate aerosol particles is modeled in this study using a 3-D chemical transport model (GEOS-CHEM). The state of these particles as aqueous or crystalline is predicted using rules based upon the extent of neutralization by ammonium and on relative humidity. Therefore, an effect of agricultural ammonia emissions is to regulate the phase of sulfate particles in the troposphere. The five particle tracers in the model include aqueous sulfate, aqueous ammonium, solid ammonium sulfate (AS), solid letovicite (LET), and solid ammonium bisulfate (AHS). Gas-phase precursors for the formation of both sulfate and ammonium are also included. The deliquescence relative humidities (DRH) for AS, LET, and AHS are 80%, 69%, and 40%, respectively. The crystallization relative humidities (CRH) for different extents of neutralization of the aqueous particles are based upon recent laboratory results. The modeling results for 2001 show that the sulfate burden by mass is partitioned as 43% solids as an average for the troposphere. The solids are 93% AS, 6% LET, and 1% AHS. 25% of the sulfate burden is present as AS in the boundary layer, 40% in the middle troposphere, and 65% in the upper troposphere. When performing a sensitivity study by increasing CRH up until it is equal to the DRH, the tropospheric solid burdens increase from 40% to 72% for AS, 2.6% to 3.6% for LET, and 0.3% to 1.8% for AHS. The partitioning between solid and aqueous particles affects radiative transfer and various chemical cycles such as N_2O_5 hydrolysis and ultimately troposphere ozone. Implications of these results for aerosol direct radiative forcing are considered.

A Review of The State-of-the-Science of Odor Assessment and Measurement

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Abstract

Odors remain at the top of air pollution complaints to regulators and government bodies around the U.S. and internationally. Ambient air holds a mixture of chemicals from everyday activities of industrial and commercial enterprises.

A person's olfactory sense, the sense of smell, gives a person the ability to detect the presence of some chemicals in the ambient air. Not all chemicals are odorants, but when they are, a person may be able to detect their presence. Therefore, an odor perceived by a person's olfactory sense can be an early warning or may simply be a marker for the presence of air emissions from a facility. For whatever reason, it is a person's sense of smell that can lead to a complaint.

When facility odors affect air quality and cause citizen complaints, an investigation of those odors may require that specific odorants be measured and that odorous air be measured using standardized scientific methods. Point emission sources, area emission sources, and volume emission sources can be sampled and the samples sent to an odor laboratory for testing of odor parameters, such as odor concentration, odor intensity, odor persistence, and odor characterization. Odor can also be measured and quantified directly in the ambient air, at the property line and in the community, using standard field olfactometry practices.

Presently, international standards are in place, which dictate the scientific methods and practices of odor measurement. These international standard methods for quantifying odor are: objective, quantitative, dependable, and reproducible.

The intent of this report is to present the basics of measuring odorous air. This paper discusses a brief overview of nasal anatomy, a review of odor testing parameters, quantification of source odor samples with laboratory olfactometry, and quantification of ambient odor with field olfactometry.

Olfactory Anatomy

Of the five senses, the sense of smell is the most complex and unique in structure and organization. While human olfaction supplies the majority of flavor sensations during eating, the olfactory system plays a paramount role as a defense mechanism by creating a natural aversion response to malodors and irritants. Human olfaction is a protective sense, protecting from potential illness of infection caused by tainted food and matter, such as rotting vegetables, putrefying meat, and fecal matter. This is accomplished with two main nerves: 1) the olfactory nerve (first cranial nerve) processes the perception of chemical odorants, and 2) the trigeminal nerve (fifth cranial nerve) processes the irritation or pungency of chemicals, which may or may not be odorants.

During normal nose breathing only a small percentage of inhaled air passes up and under the olfactory receptors in the top, back of the nasal cavity. When a sniffing action is produced, either an involuntary sniff reflex or a voluntary sniff, a significantly greater amount of inhaled air is carried to the area near the olfactory receptors due to turbulent action in front of the turbinates. These receptors, in both nasal cavities, are ten to twenty-five million olfactory cells making up the olfactory epithelium. Cilia on the surface of this epithelium have a receptor contact surface area of approximately five square centimeters due to the presence of many microvilli on their surface. Supporting cells surrounding these cilia secrete mucus, which acts as a trap for chemical odorants.

Chemical odorants pass by the olfactory epithelium and are dissolved into the mucus at a rate dependent on their water solubility and other mass transfer factors. The more water-soluble the chemical, the more easily it is dissolved into the mucus layer. Sites on the olfactory cells, assisted by specialized proteins, receive the chemical odorant. The response created by the reception of a chemical odorant depends on the mass concentration, i.e. the number of odorant molecules. Each reception creates an electrical response of the olfactory nerves. A summation of these electrical signals leads to an action potential. If this action potential has high enough amplitude (i.e. threshold potential), then the signal is propagated along the nerve where it synapses with the olfactory bulb.

All olfactory signals meet in the olfactory bulb where the information is distributed to two different parts of the brain. One major pathway of information is to the limbic system, which processes emotion and memory response of the body. The second major information pathway is to the frontal cortex. This is where conscious sensations take place as information is processed with other sensations and is compared with cumulative life experiences for the individual to possibly recognize the odor and make some decision about the experience.

Frequently the terms odor and odorant are used interchangeably and, often incorrectly. There is a distinct difference between these two terms, which is fundamental to the discussion of odor and odor nuisance. The term odor refers to the perception experienced when one or more chemical substances in the air come in contact with the various human sensory systems (odor is a human response). The term odorant refers to any chemical in the air that is part of the perception of odor by a human (odorant is a chemical). Odor perception may occur when one odorant (chemical substance) is present or when many odorants (chemical substances) are present.

Laboratory Olfactometry

Overview of Odor Parameters

Odor is measurable using scientific methods. Odor testing has evolved over time with changes in terminology, methods, and instrumentation.

Four measurable, objective parameters of perceived odor are:

1) **Odor Concentration** – measured as dilution ratios and reported as detection threshold and recognition thresholds or as dilution-to-threshold (D/T) and sometimes assigned the pseudo-dimension of odor units per cubic meter.
2) **Odor Intensity** – reported as equivalent parts per million butanol, using a referencing scale of discrete concentrations of 1-butanol (n-butanol).
3) **Odor Persistence** – reported as the dose-response function, a relationship of odor concentration and odor intensity.
4) **Odor Character Descriptors** - what the odor smells like using categorical scales and real exemplars.

These odor parameters are objective because they are measured using techniques or referencing scales dealing with facts without distortion by personal feelings or prejudices.

Additional measurable, but subjective, parameters of perceived odor are:

1) **Hedonic Tone** - pleasantness vs. unpleasantness.
2) **Annoyance** - interference with comfortable enjoyment of life and property.
3) **Objectionable** - causes a person to avoid the odor or causes physiological effects.
4) **Strength** - word scales like “faint to strong”.

These odor parameters are subjective because individuals rely on their interpretation of word scales and their personal feelings, beliefs, memories, experiences, and prejudices to report them. Written guidelines for subjective odor parameter scales assist individuals (citizens and air pollution inspectors) in reporting observed odor, however, the nature of these parameters remains subjective.

Odor Panels

The origins of sensory evaluation and nasal organoleptic testing are in the trade industry. Products such as perfumes, coffee, tea, wine, liquors, meats and fish were smelled or tasted to determine the quality of the product. Eventually, individuals became known as expert judges and were used to rate or grade products.

In the 1940's and 1950's great advancements took place in sensory testing by researchers performing sensory evaluation for developers of U.S. government war rations. Since that time, panels of trained sensory assessors have been the preferred method of evaluating sensory characteristics of products in a laboratory setting.

In the field of environmental engineering, odorous air samples can be collected from emission sources. Odor evaluation of odorous air samples is conducted under controlled laboratory conditions following standard industry practices using trained panelists known as assessors.

Odor assessors are recruited from the community at large. Odor panels consist of assessors that are selected and trained following the "Guidelines for Selection and Training of Sensory Panel Members" (ASTM Special Technical Publication 758) and EN13725 (ASTM, 1981; CEN, 2003).

Each odor assessor is tested to determine their individual olfactory sensitivity using standard odorants, e.g. n-butanol and hydrogen sulfide. The assessor receives training that consists of olfactory awareness, sniffing techniques, standardized descriptors, and olfactometry responses. Odor sensitivity and performance parameters of the assessors are continually monitored under detailed QA/QC programs.

Determination of Odor Concentration in the Laboratory

The most common odor parameter determined by odor testing is odor concentration. Odor concentration is determined using an instrument called an olfactometer and is expressed as a dilution factor (dilution ratio). Odor concentration is reported as the Detection Threshold (DT) and Recognition Threshold (RT). Several advances in technology and standard practice have changed the science of olfactometry over the last 50 years and the new millennium began with the publication of a new internationally accepted standard for determination of odor concentration.

In the 1950's, sensory evaluation in the laboratory came into practice to quantify the strength of odorous air emissions. Laboratory olfactometry involves diluting the odorous air sample at varying concentrations then presenting the diluted odor to human assessors to determine the threshold of the odorous emission. The laboratory dilution process simulates the dilution of the odor in the ambient air.

In 1957, the ASTM International E-18 Sensory Evaluation Committee approved and published a method for measuring environmental odors in a laboratory setting (Mills et. al., 1963). The ASTM standard D1391 was called, "Measurement of Odor in Atmospheres" (ASTM, 1978). The D1391 standard came to be known as the syringe static dilution method because it used 100-mL glass syringes to dilute the odorous air with odor free air. The practice involved presenting assessors syringes of diluted odorous air samples along with syringes of odor-free air. The assessors would then report which syringe contained the odor sample (Benforado, 1969).

The cumbersome nature of this static dilution method led to the development of dynamic olfactometers, which were designed to perform the dilutions of the odorous air automatically and continuously.

In 1979, ASTM International published E679-79, "Standard Practice for Determination of Odor and Taste Thresholds by a Forced-Choice Ascending Concentration Series Method of Limits." This method was based on the use of dynamic olfactometry to automatically perform the dilutions of the odorous air and then immediately present the dilution mixture to the human assessors. In March 1985, the ASTM E18 Committee officially withdrew the "Syringe Method", D1391, from publication. The dynamic dilution method, E679, was subsequently revised in late 1991, re-approved in 1997, and again revised in 2004. The 2004 procedural revisions were minor, however, two additional testing examples were added to the appendix.

The ASTM E679 procedure is based on a presentation method called 3-alternative forced-choice (3-AFC) or triangular forced-choice (TFC). Each assessor performs the odor evaluation task by sniffing the diluted odor from an olfactometer. The assessor sniffs three sample presentations; one contains the diluted odor while the other two are blanks (odor-free air). Figure 1 shows one assessor (left) sniffing from the olfactometer nasal mask while the test administrator (right) operates the olfactometer. The assessor is required, or forced, to choose one of the three presentations. The assessor acknowledges their choice as a guess, a detection or recognition. As defined by E679, a response of detection is determining the selection is different from the other two, and a recognition response is that the selected presentation smells like something.

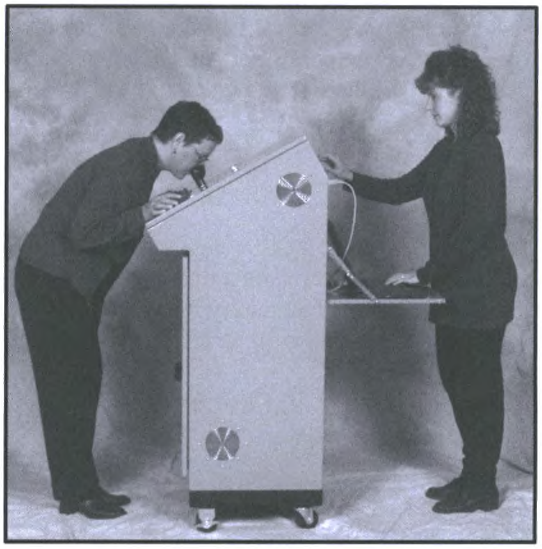

Figure 1. Assessor (left) sniffing at a dynamic dilution olfactometer. AC'SCENT Olfactometer photo courtesy of St. Croix Sensory, Inc.

The assessor is then presented with the next dilution level. The assessor is again presented with three sample choices, one of which is the diluted odor sample. However, this next dilution level presents the odor at a higher concentration (e.g. two times higher). This is one-half the dilution ratio. The first dilution level presented to the assessors is below the odor thresholds (sub-threshold). The assessor proceeds to higher levels of sample presentation following these methods. The statistical approach of increasing the concentration is called "ascending concentration series."

The convention of calculating dilution factors for olfactometry is based on the ratio of Total Volumetric Flow to the Odorous Sample Flow (Turk, 1973; Dravnieks et. al., 1979, 1980, 1986; ASTM, 1978 1991, 2004; AWMA, 1995, CEN, 2003):

$$\text{Dilution Factor} = \frac{V_d + V_o}{V_o} = Z$$

Where V_d is the volumetric flow rate of odor-free, dilution air and V_o is the volumetric flow rate of the odorous air sample. The dilution factor, 'Z', is used in modest honor of H. Zwaardemaker, a Dutch scientist and early investigator in olfactometry. The odor concentration is a number derived from the panel of assessors' responses to the laboratory dilution of odorous air samples.

Alternative terminology in use includes: Dilution-to-Threshold Ratio (D/T), Odor Unit (OU), and Effective Dose at 50% of the population (ED50) (ASTM, 2004).

A large dilution ratio (e.g. 65,000) represents a high dilution of the odor sample. A high dilution of odor is similar to a person standing at a great distance from the odorous emissions. A small dilution ratio (e.g. 8) represents a small dilution of the odor sample. A small dilution of the odor is similar to a person standing close to the odorous emissions.

The odor concentration results from olfactometry testing are expressed as a detection or recognition threshold. The detection threshold (DT) is an estimate of the number of dilutions needed to make the actual odor emission non-detectable. The recognition threshold (RT) represents the number of dilutions needed to make the odor sample faintly recognizable.

A detection threshold for an odorous air sample is larger than its recognition threshold value, because more dilutions with odor-free air are needed to make the odor non-detectable compared to making the odor faintly recognizable. A large value of odor concentration (DT or RT) represents a strong odor. A small value for odor concentration represents a weak odor.

International Standardization of Odor Concentration Measurement

During the 1980's, countries in Europe, such as France (AFNOR X-43-101), Germany (VDI 3881), and The Netherlands (NVN 2820), began developing standards of olfactometry. In the 1990's a working group formed within the Comité Européen de Normalisation (CEN), Technical Committee 264 – "Air Quality", to develop a unified European olfactometry standard.

The first complete draft of the European olfactometry standard was released in 1995. The standard was published in 2003 as CEN standard #13725 (EN13725) "Air Quality – Determination of Odour Concentration by Dynamic Olfactometry" (CEN, 2003).

The approval of this CEN standard, EN13725, obligates all countries of the European Union to adopt the standard and withdraw any conflicting or redundant national standards.

The new European standard has also been adopted by Standards Australia and Standards New Zealand as AS/NZS 4323.3:2001 (AS, 2001). The standard has also been referenced by national organizations in Singapore, Thailand, and several other S.E. Asian countries. Furthermore, government agencies and universities throughout North America are following or are working towards adoption of the EN13725 standard. Examples of the government agencies include: Agriculture Canada, City of Los Angeles, Los Angeles County, and Metropolitan Council in St. Paul, Minnesota. Examples of the universities include: Duke University, Iowa State University, Purdue University, University of Alberta, University of Manitoba, and University of Minnesota.

Therefore, EN13725 has become the de facto international standard for odor testing.

Odorous Air Dispersion Modeling

Odor concentration is an estimate of the number of dilutions needed to make the actual odor emission non-detectable. The dilution of the actual odor emission is the physical process that occurs in the atmosphere down wind of the odor source(s). The receptor (citizen in the community) sniffs the ambient air that has the diluted odor. If the receptor detects the odor, then the odor in the ambient air is said to be at or above the receptor's detection threshold level for that odor.

Odor concentration values are dilution factors (dilution ratios) and are, therefore, dimensionless values. However, the pseudo-dimension of odor units per cubic meter is commonly used for odor dispersion modeling, taking the place of grams per cubic meter in the air dispersion model. This odor concentration value can then be multiplied by the airflow rate of the emission source, i.e. cubic meters per second, resulting in the pseudo-dimension of odor units per second for the odor emission rate, analogous to grams per second in the air dispersion model.

Because odor concentration values are actually dimensionless, odor concentration from different sources cannot be added nor can they be averaged. Therefore, odor modeling must be conducted with caution. Air dispersion models typically have outputs of concentration (e.g. micrograms per cubic meter) at specific receptors or plotted as isopleths. These standard modeling outputs need to be converted to the pseudo-dimension odor units per cubic meter with proper treatment of the decimal place. The resulting odor concentration value of 1–odor unit per cubic meter, calculated by the dispersion model, represents the odor detection threshold. A value less than "1" represents no odor or sub-threshold and a value greater than "1" represents odor at supra-threshold.

Odor model approaches assist in decision making to identify and mitigate odors. Further, an odor regulation or permitting process might use odor (air) dispersion modeling to back-calculate an emission source maximum (i.e. odor concentration) from ambient odor criteria, i.e. '4' or '7' D/T ("dilution-to-threshold" or "odor units per cubic volume").

Odor Intensity

Perceived odor intensity is the relative strength of the odor above the recognition threshold (suprathreshold). ASTM E544-99, "Standard Practice for Referencing Suprathreshold Odor Intensity," presents two methods for referencing the intensity of ambient odors to a standard scale: Procedure A – Dynamic-Scale Method and Procedure B – Static-Scale Method. The Dynamic-Scale Method utilizes an olfactometer device with a continuous flow of a standard odorant (n-butanol) for presentation to an assessor. The assessor compares the observed intensity of an odorous air sample to a specific concentration level of the standard odorant from the olfactometer device. The Static-Scale Method utilizes a set of bottles with fixed dilutions of a standard odorant in a water solution (Turk, 1980).

Butanol concentrations are a referencing scale for purposes of documentation and communication in a reproducible format. For this method, the odor intensity result is expressed in parts per million (PPM) of n-butanol. A larger value of butanol means a stronger odor. A small value of butanol means a weaker odor.

Odor Persistency

Odor is a psychophysical phenomenon. Psychophysics involves the response of an organism to changes in the environment perceived by the five senses (Stevens, 1960). Examples of psychophysical phenomenon include how the human body perceives sound loudness, lighting brightness, or odor intensity.

In the 19th Century, E.H. Weber proposed that the amount of increase in a physical stimulus, to be just perceivably different, was a constant ratio. This relationship can be expressed as:

$$\Delta I/I = \Delta C/C = k$$

Where I is the stimulus intensity, C is the measurable amount or concentration of stimulus, and k is a constant that is different for every sensory property and specific stimulus.

As an example, this expression means that there would be the same perceived increase in intensity when changing a concentration of sugar in water from 10% to 11% as when changing the concentration from 20% to 22%.

In the 1950's and 1960's, through his work at Harvard University, S.S. Stevens proposed that apparent odor intensity grows as a power function of the stimulus odorant. Stevens showed that this Power Law (Steven's Law) follows the equation (Stevens, 1957, 1962):

$$I = k\,C^n$$

Where I is the odor intensity, C is the mass concentration of odorant (e.g. mg/m^3), and k and n are constants that are different for every specific odorant or mixture of specific odorants.

As shown in Figure 2, this equation is a straight line when plotted on a log-log scale. The x-axis is the mass concentration (mg/m3) of the single odorant. The upward slope of the graph illustrates that the odor intensity of the single odorant increases as the mass concentration increases. Steven's Law has been used most often in modern odor science (Dravnieks, 1979; O'Brien, 1991; Prokop, 1992).

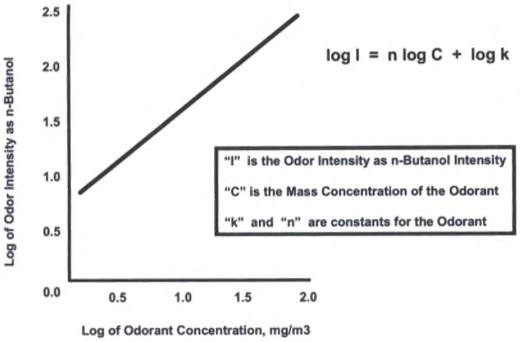

Figure 2. Power law graph of a single odorant.

Odor Persistency is a term used to describe the rate at which an odor's perceived intensity decreases as the odor is diluted (i.e. in the atmosphere downwind from the odor source). Odor intensities decrease with dilution at different rates for different odors. Figure 3, illustrates how odor intensity decreases as the odor is diluted.

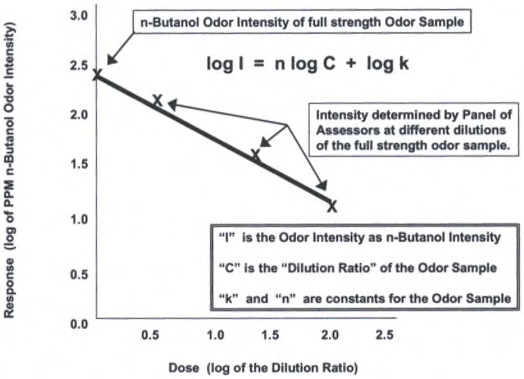

Figure 3. "Dose-Response" graph of an odor sample.

The Dose-Response function is determined from intensity measurements of an odor at various dilutions and at full strength (Dravnieks, 1980). Plotted as a straight line on a log-log scale, the result is a linear equation specific for each odor sample. The slope of the line represents the relative persistency. The logarithm of the constant k is related to the intensity of the odor sample at full strength (Dravnieks, 1986).

Note that comparing Figure 2 to Figure 3, Figure 2 has a positive slope, because the concentration (x-axis) is the mass concentration in mg/m^3 of the odorant, e.g. hydrogen sulfide. The log-log plot in Figure 3 has a negative slope because the concentration (x-axis) is the dilution ratio of an odor sample.

Other researchers have investigated other relationships between odor intensity and dilution ratios (Cain et. al., 1974; Chen et. al., 1999).

Odor Characterization

Descriptive analysis is a sensory science term used to describe the action of a panel of assessors describing attributes about a product or sample (qualitative) and scaling the intensity of these attributes (quantitative). The food, beverage, and consumer product industries have formally used descriptive analysis to obtain detailed information about the appearance, aroma, flavor, and texture of products for well over 50 years.

Odor character, often called odor quality, is a nominal scale of measurement. Odors can be characterized using a reference vocabulary. Standard practice has been to provide assessors with a standard list of descriptor terms, which are organized with like terms in groups. Similarly, terms with negative connotation (unpleasant) would be grouped with other negative terms and positive (pleasant) terms with other positive terms (Harper, 1968; Dravnieks, 1985).

Applicability of Laboratory Olfactometry

When odor is present in the ambient air and causes citizens to complain, investigation by trained personnel is prescribed. Investigators verify citizen complaints through actions of complaint response and surveillance of the probable sources of odor. Laboratory olfactometry often is a part of or follows field odor investigations and studies.

The collection of whole-air odor samples and the testing of the samples in an odor (olfactometry) laboratory may be:

1) Part of a developing investigation (i.e. enforcement actions),
2) Part of an odor study (i.e. comparing or ranking odorous processes),
3) Part of an odor control system performance test (i.e. manufacturer's guaranty), or
4) Part of a routine performance test at a facility (i.e. compliance test required by permitting authorities).

Engineers, managers, and regulators who are planning odor mitigation can use the results of laboratory odor testing to assist in their decision-making.

Field Olfactometry

Odor can also be measured and quantified directly in the ambient air by trained inspectors using a field olfactometer, which dynamically dilutes the ambient air with carbon-filtered air in distinct dilution ratios known as Dilution-to-Threshold dilution factors (D/T's).

Olfactory Performance of Odor Inspectors

An odor inspector's olfactory sensitivity is a factor when using field olfactometry methods to measure odor in the ambient air. A standardized nasal chemosensory test method would determine the olfactory threshold of an individual (e.g. odor inspector) and allows comparison of the individual's olfactory sensitivity to normative values (normal olfactory thresholds).

In the routine clinical evaluation of patients with olfactory disorders, one commercially available psychophysical testing method is known as Sniffin' Sticks. Sniffin' Sticks, manufactured by Burghart of Germany, are odor-dispensing felt tip marker pens. One nasal chemosensory testing mode can determine a person's odor threshold based on the standard odorant n-butanol.

A published multi-clinic investigation of 1,000 subjects, tested with the odor pen kit, provides normative test result values for the general population (Kobal, et. al., 2000). A study conducted by St. Croix Sensory in 2003 confirmed the results of this study and were used to develop performance criteria for field inspectors (Lay, et. al., 2004).

It is assumed that olfactory sensitivity varies as a result of random fluctuations in factors such as alertness, attention, fatigue, health status, and the possibility of variable presentation techniques of the testing stimulus source. Therefore, even though the determination of an individual's olfactory threshold is a definable task, the precision of the result is based on the number of times the individual takes the test. Further, an individual's general condition of health, i.e. common cold and seasonal allergies, needs to be considered in the timing and applicability of the testing.

Ambient Odor Concentration (D/T) with Field Olfactometers

In 1958, 1959, and 1960 the U.S. Public Health Service sponsored the development of an instrument and procedure for field olfactometry (ambient odor strength measurement) through Project Grants A-58-541; A-59-541; and A-60-541 (Huey, et. al., 1960). The first field olfactometer, called a Scentometer, was manufactured by the Barnebey-Cheney Company and subsequently manufactured by the Barnebey Sutcliffe Coporation.

A field olfactometer creates a series of dilutions by mixing the odorous ambient air with odor-free (carbon-filtered) air. The U.S. Public Health Service method defined the dilution factor as Dilution to Threshold, D/T. The Dilution-to-Threshold ratio is a measure of the number of dilutions needed to make the odorous ambient air non-detectable.

The method of producing Dilution to Threshold (D/T) ratios with a field olfactometer consists of mixing two volumes of carbon-filtered air (two carbon filters) with specific volumes of odorous ambient air. Figure 4 is a block diagram which illustrates the mixing of carbon-filtered air with odorous air in a field olfactometer.

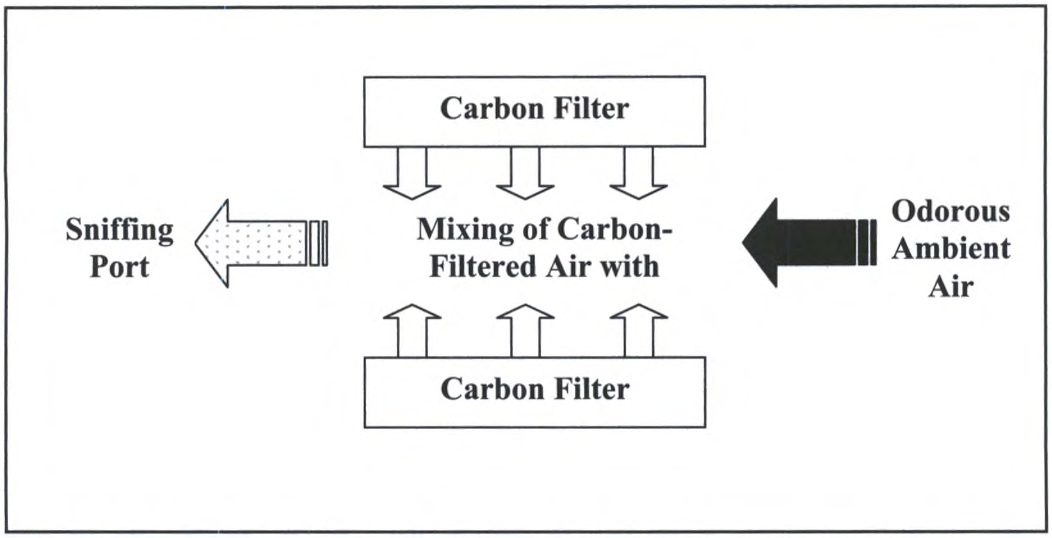

Figure 4. Block diagram of field olfactometer air flow.

The method of calculating Dilution to Threshold (D/T) for a field olfactometer is:

$$\text{Dilution Factor} = \frac{\text{Volume of Carbon Filtered Air}}{\text{Volume of Odorous Air}} = \mathbf{D/T}$$

Note that the calculation method for field olfactometry is different from the calculation of the dilution factor in laboratory olfactometry. The calculation difference is illustrated in the following example:

A field olfactometer uses 7 volumes of carbon-filtered air to one volume of odorous air:

$$\frac{7}{1} = 7 \quad \text{(D/T Value)}$$

A laboratory olfactometer uses 7 volumes of carbon-filtered air to one volume of odorous air:

$$\frac{7+1}{1} = 8 \quad \text{(Z value)}$$

Two commercially available field olfactometers include the original Scentometer, developed in the late 1950's, and the Nasal Ranger®, introduced to the market in 2002.

Scentometer Field Olfactometer

The Barnebey Sutcliffe Corporation Scentometer, shown in Figure 5, is a rectangular, clear plastic box (15.25cm x 12.7cm x 6.2cm) containing two activated carbon beds. The box contains two ½" diameter air inlets to the activated carbon beds (one on top and one on the bottom of the box). There are six odorous air inlet holes on one end of the box for six different D/T values (2, 7, 15, 31, 170, and 350). The opposite end of the box contains two glass nostril tubes for sniffing.

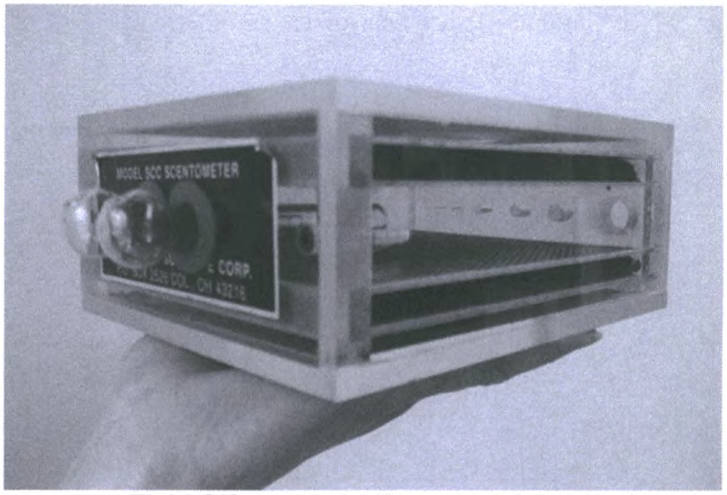

Figure 5. The Scentometer Field Olfactometer (Barnebey Sutcliffe Corp.). Note the two glass nostril ports to the left and the series of orifice holes at the back of the unit to the right in this photo.

Nasal Ranger Field Olfactometer

The St. Croix Sensory - Nasal Ranger Field Olfactometer, shown in Figure 6, operates based on the same principles as the original Scentometer Field Olfactometer. Carbon-filtered air is supplied through two replaceable carbon cartridges. An orifice selector dial on the Nasal Ranger contains six odorous air inlet orifices for six different D/T values (2, 4, 7, 15, 30, and 60). The dial contains six "blank" positions (100% carbon-filtered air) alternating with the D/T orifices. The dial is replaceable for other D/T series (e.g. 60, 100, 200, 300, 500).

The diluted odorous air is sniffed through an ergonomically designed nasal mask, which is constructed of a carbon fiber/epoxy blend with a fluoropolymer (Teflon-like) coating. A check valve is placed in both the inhalation and exhalation outlet of the nasal mask to control the direction of airflow while using the Nasal Ranger.

The Nasal Ranger is designed with an airflow sensor that measures the inhalation/sniffing flow rate through the field olfactometer. The measured flow is continually compared to design specifications and feedback is provided to the user through LED's mounted on the top of the unit. The user must inhale/sniff at a rate where the LED's show the total airflow is in the Target range (nominal 16-20 LPM). This feedback loop standardizes the inhalation/sniffing rate for all users of this field olfactometer and allows for certified traceable calibration of the Nasal Ranger.

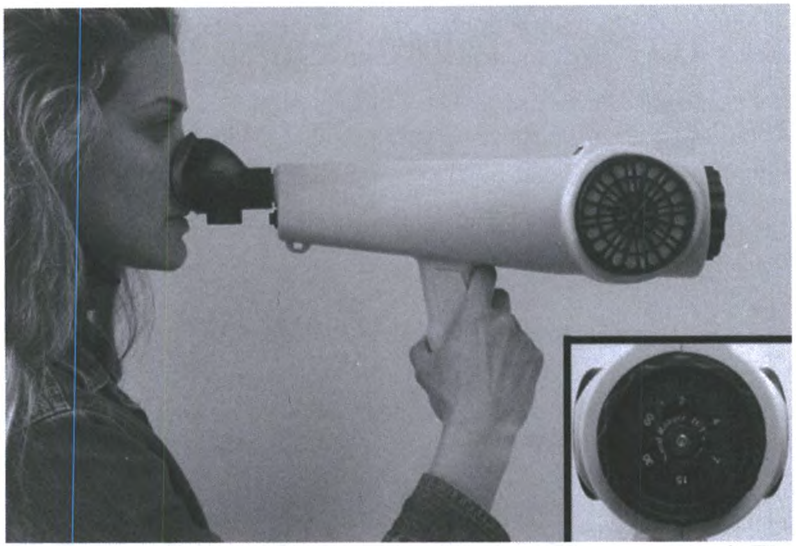

Figure 6. The Nasal Ranger® Field Olfactometer (St. Croix Sensory, Inc.). The inset picture shows a close-up of the orifice dial, which is located at the right side of the Nasal Ranger in this photo.

The field olfactometer instrument, the "Dilution to Threshold" (D/T) terminology, and the method of calculating the D/T are referenced in a number of existing state and local agencies' odor regulations and permits. Therefore, a field olfactometer is a realistic and proven method for quantifying ambient odor strength when used by trained air pollution inspectors or monitors.

Common Dilution-to-Threshold (D/T) ratios used to set ambient odor guidelines are:

D/T's of 2, 4, and 7. Field olfactometers typically have additional D/T's (dilution ratios) such as 15, 30, 60 and higher dilution ratios.

Field olfactometry is a cost effective means to quantify odors. Facility operators, community inspectors, and neighborhood citizens can confidently monitor odor strength at specific locations around a facility's property line and within the community.

Conclusions

Odor is measurable using standardized scientific methods in odor-testing laboratories with laboratory olfactometry and in the ambient air with field olfactometry. Point, area and volume emission sources can be sampled and tested for odor parameters such as odor concentration, intensity, persistence, and descriptors. Odor can also be measured and quantified directly in the ambient air by trained inspectors utilizing calibrated field olfactometers, which dynamically dilute ambient air with carbon-filtered air in distinct dilution ratios known as Dilution-to-Threshold dilution factors (D/T's).

Presently, international standards are in place, which dictate the scientific methods and practices of odor measurement. These international standard methods for measuring odor are objective, quantitative, dependable, and reproducible. These standards include:

1) From ASTM International:
    a) ASTM E679-04: *Standard Practice for Determination of Odor and Taste Threshold by a Forced-Choice Ascending Concentration Series Method of Limits*
    b) ASTM E544-99: *Standard Practice for Referencing Suprathreshold Odor intensity*
2) From the Comité Européen de Normalisation (CEN)
    a) EN13725:2003: *Air Quality – Determination of Odour Concentration by Dynamic Olfactometry*

With these standard odor measurement practices, odor limits may be incorporated into odor regulations or into facility permits as compliance determining criteria with confidence. This can be done with ambient odor limits based on odor concentration (D/T) or on source odor limits based on either the odor concentration (odor units per cubic meter) or odor emission rates (odor units per second). Note that these basic odor limits are not mutually exclusive and are sometimes combined.

The stakeholders for standardized odor measurement include regulators, industries, citizens, manufacturers of environmental control equipment, consultants, and researchers. With the knowledge of fundamental odor testing methods and practices, an objective approach can be taken to address community nuisance odors and problematic odorous emissions. The subjectivity of "nuisance odors" can be replaced with objective, scientific methods of odor measurement with laboratory olfactometry and field olfactometry.

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Agricultural Emissions of Greenhouse Gases in Croatia

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Abstract

The Republic of Croatia is a signatory to the Kyoto Protocol. Upon its entering into force and its ratification by Parlament, Croatia shall commit to reduce its emissions of GHG by 5 percent in relation to the reference year, over the commitment period from 2008 to 2012. Agricultural activities contribute directly to emissions of greenhouse gases and are seen as a source with great potential in reducing them. Methane (CH_4) and nitrous oxide (NO_2) are the primary greenhouse gases emitted by agricultural activities. On the basis of the best available activity data, emissions were estimated for the period from 1990 – 2003, in accordance with methodology prescribed by the scientific body of the Convention (Intergovernmental Panel on Climate Change – IPCC).

1. Agricultural Methane (CH_4) Emission

1.1. Methane (CH_4) Emission – Enteric Fermentation

Methane is a direct product of animal metabolism generated during the digestion process. The greatest producers of methane from enteric fermentation in Croatia are ruminants (cows, cattle, and sheep). The amount of methane produced and excreted depends on the animal digestive system and the amount and type of the animal feed. Figure 1 shows the emission of methane from enteric fermentation for the period from 1990-2003. The estimates in this inventory include only emissions for farm animals. CH_4 emission from enteric fermentation is a key source, both by level and trend. Dairy cattle is the single major source of emissions represent more than 50% of total CH_4 emissions from enteric fermentation, followed by non dairy cattle represent about 30% of total CH_4 from enteric fermentation.

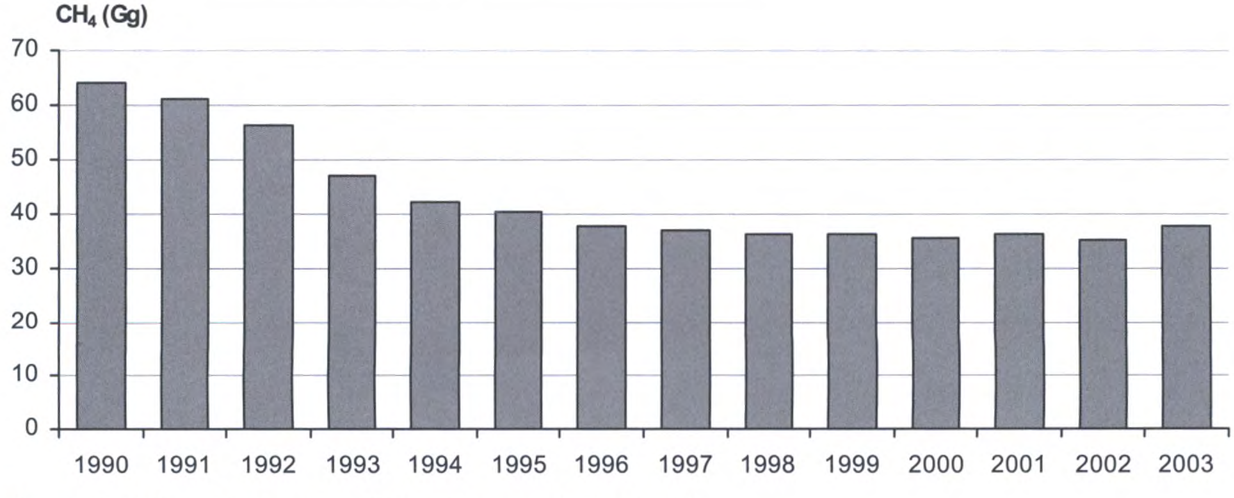

Figure 1 - CH_4 emission from Enteric fermentation (Gg)

1.2. Methane (CH_4) Emission - Manure Management

Methane is generated under the conditions of anaerobic decomposition of manure. Storing methods of the manure in which the anaerobic conditions prevails (liquid animal manure in septic pits) are favourable for anaerobic decomposition of organic substance and release of methane. Methane emission from manure management for the period from 1990 to 2003 is given in the Figure 2.

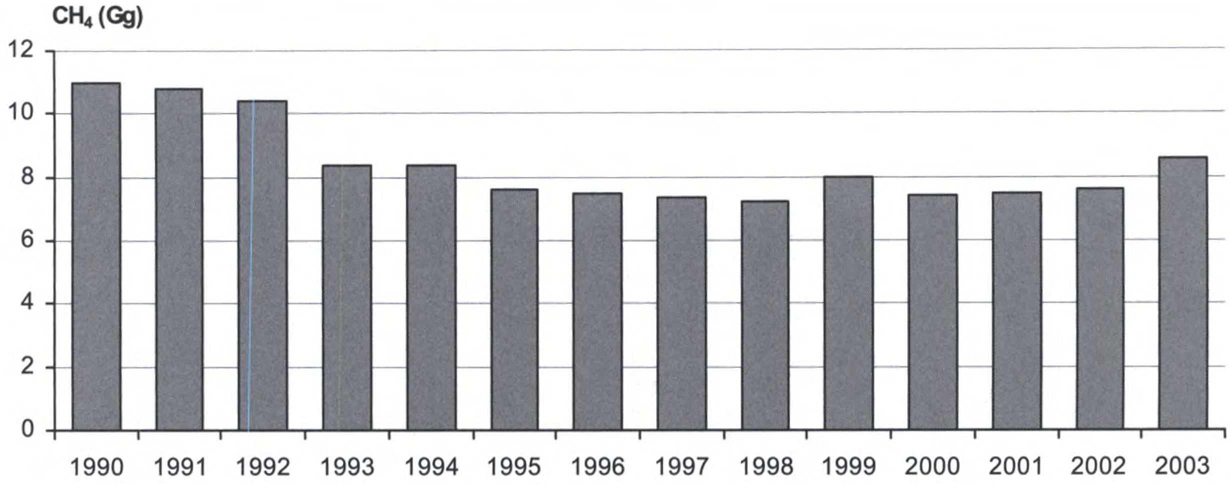

Figure 2 - CH_4 emission from Manure Management (Gg)

2. Agricultural N_2O Emission

2.1. N_2O Emissions from Manure Management

The emissions of nitrous oxide (N_2O) from all animal waste management systems are estimated. This includes emissions from anaerobic lagoons, liquid systems, solid storage, dry lot, and other systems. The N_2O emissions from pasture range and paddock are reported under Agricultural soils. The nitrous oxide (N_2O) emissions from manure management for the period from 1990 to 2003 are shown on figure 3.

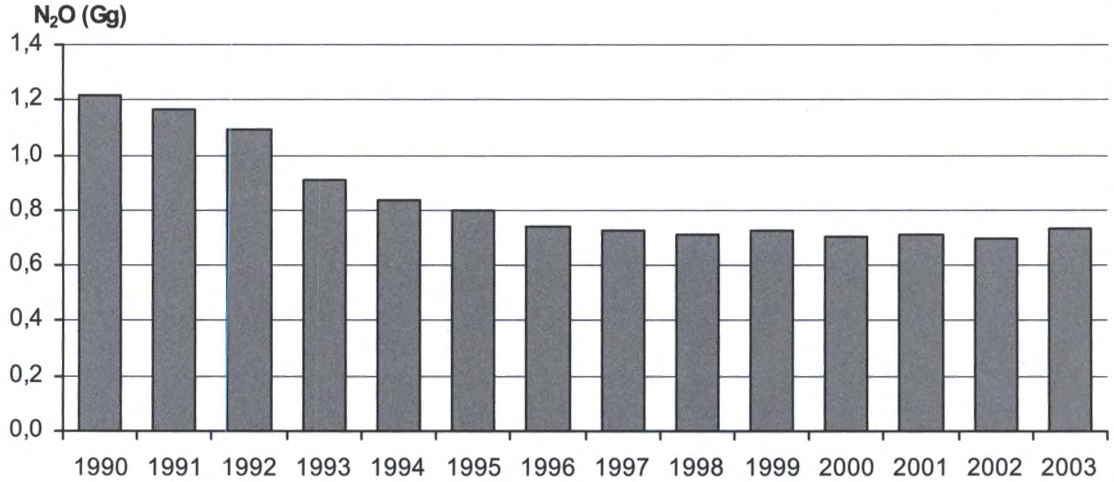

Figure 3 - N_2O Emissions from Manure Management (Gg)

2.2. Direct N_2O Emissions from Agricultural Soils

Direct emissions N_2O from agricultural soils includes total amount of nitrogen applied to soils through cropping practices. These practices includes application of synthetic fertilizers, nitrogen from animal waste, production of nitrogen–fixing crops, nitrogen from crop residue mineralization, and soil nitrogen mineralization due to cultivation of histosols. The input data required for this part of the calculation were:

annual quantity of the synthetic fertilizer used, the quantity of organic fertilizer, the head of animals by its category, the biomass of leguminous plants and soybean, and the surface of histosols. Figure 4 shows direct emission of nitrous oxide from agricultural soils (1990 – 2003).

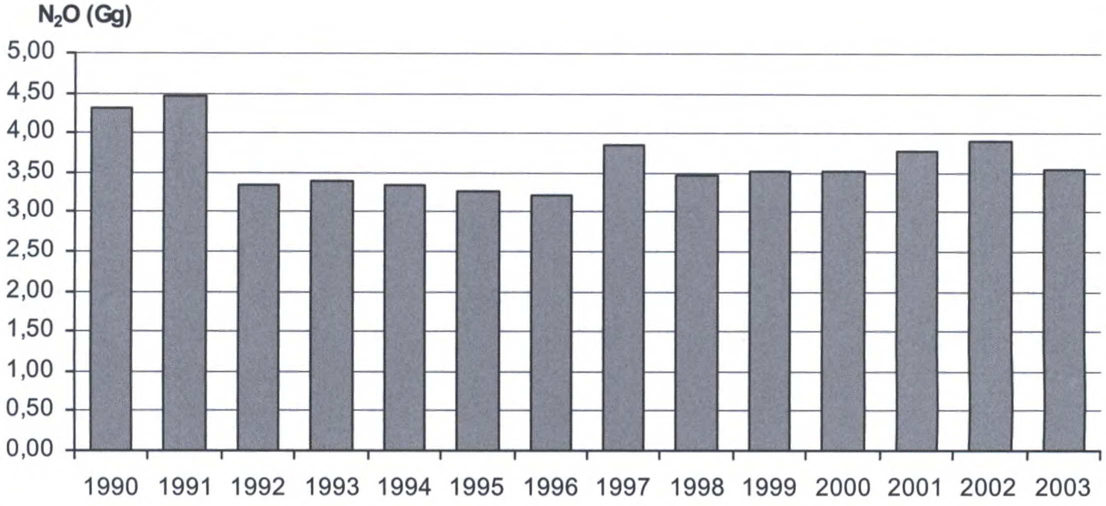

Figure 4 - Direct N_2O Emissions from Agricultural Soils (Gg)

2.3. Direct Emission of N_2O from Animals

Estimates of N_2O emissions from animals were based on animal waste deposited directly on soils by animals in pasture, range and paddock. The same emission factor (0.02 kg N_2O-N/kg of emitted N) suggested by IPCC (1996) was used for all grazing animals, regardless of their species and climatic conditions. Figure 5 shows direct emission of nitrous oxide from animals (1990 – 2003).

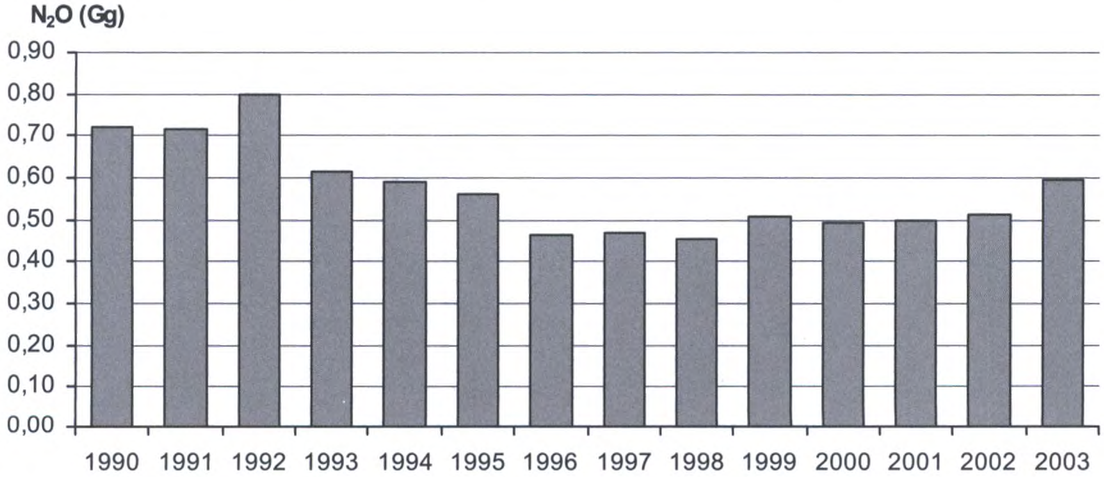

Figure 5 - Direct N_2O Emissions from Animals (Gg)

2.4. Indirect N_2O Emissions from Nitrogen Used in Agriculture

Calculations of indirect N_2O emissions from nitrogen used in agriculture are based on two pathways. These are: volatilization and subsequent atmospheric deposition of NH_3 and NO_x (originating from the application of fertilizers and animal manure), and leaching and runoff of the N that is applied to, or deposited on soils.

These two indirect emission pathways are treated separately, although the activity data used are identical. Figure 6 shows the indirect emission of nitrous oxide from agriculture (1990 – 2003).

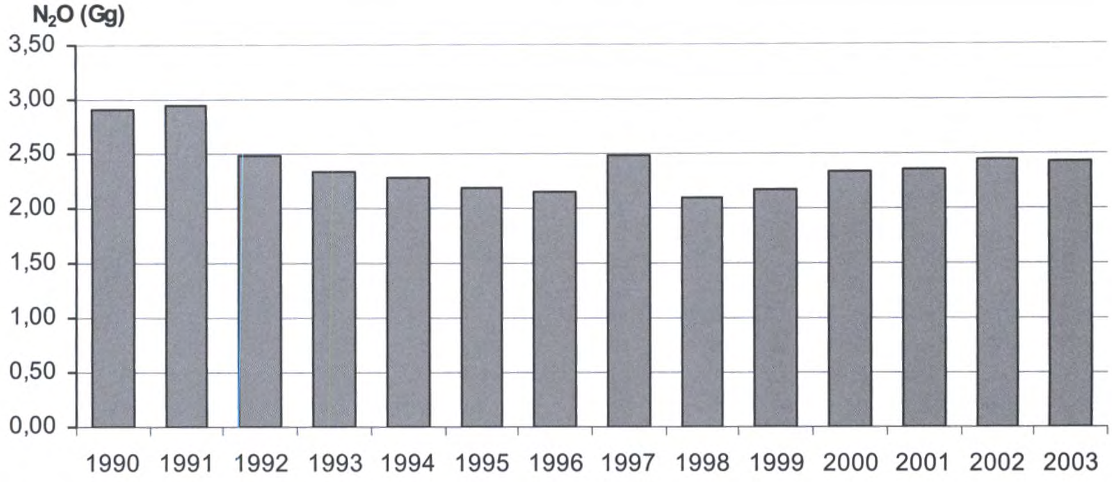

Figure 6 - Indirect N_2O Emissions from Agricultural (Gg)

3. Conclusion

Methane emissions from enteric fermentation and manure management represent 41 percent of total CH4 emissions (in year 1990.) from anthropogenic activities, respectively. Of all domestic animal types, dairy cattle were by far the largest emitter of methane. Agricultural soil management activities such as fertiliser application and other cropping practices were the largest source of Croatian N2O emissions, accounting for 70 percent of the total emission.

Key words: Climate Change, Agriculture, Methane, Nitrous Oxide

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Concurrent Measurement of Litter Gas Flux and Nutrients with Air and Litter Properties in Poultry Houses to Improve Emission Estimates

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Abstract

Accurate predictive models for animal feeding operation air emissions require inclusion of a wide range of conditions. For broiler chickens, management practices vary considerably, complicating emission measurements. This research characterized the spatial variability of litter gas flux including ammonia, nitrous oxide, carbon dioxide, and methane as well as litter nutrients, such as total Kjeldahl nitrogen, water extractable phosphate, ammonium, and nitrate, in two solid sidewall commercial broiler houses where 12 flocks were previously grown. In the 146 m by 12.8 m houses, grid samples (36 points) at 5 m across and 12 m down the house were taken during a winter flock on day 2 and 45. On day 45, eight additional samples were taken near the feeders and waterers (F/W). Gas flux estimates at each site were derived from timed gas concentrations measured using a photoacoustic multigas analyzer and an inverted chamber. Geostatistical contour plots indicate ammonia flux on day 2 was elevated in the brood area of house one (H1) where litter and air temperatures were highest. For this date, a commercial litter treatment in the brood area of house two (H2) held the ammonia flux near zero for approximately 45% of the brood area. Day 45 ammonia flux levels were similar in each house; averaging in H1 694 vs. 644 mg m^{-2} hr^{-1} in H2. Both houses exhibited a region of greater ammonia flux near the cooling pads. Ammonia flux, litter moisture and pH were diminished at the F/W locations whereas nitrate levels were elevated. Low moisture is suspected as a result of addition of dry matter from feed spillage. On day 45, an area of extensive cake near the exhaust fans in H2 provided the lowest recorded litter pH, highest moisture and ammonium in addition to essentially zero ammonia flux. For broiler health, pathogen persistence makes high litter moisture undesirable. The results indicate that house management and bird activity influence litter gas flux and nutrient level. General data trends agree with established relationships for the influence of pH, moisture, and temperature on gas emissions. However, irregular physical conditions of the litter must be considered. Input from broiler managers is required to evaluate potential management practices to prevent detrimental effects on the birds.

Introduction

In U.S. commercial poultry production, meat-type birds or broilers are usually reared on an organic bedding material (i.e. wood shavings, rice hulls). The combination of deposited manure and urine, bedding material, feathers, spilled feed and water is called "litter." Further, in high traffic areas, near the feeders and waterers or near the exhaust fans, a usually high moisture, compacted layer forms over the litter, which is known as "cake." Although the fundamental relationships among litter pH, moisture, and uric acid nitrogen (N) are known (Gates et al., 1997), the lack of homogeneity of the litter creates difficulty in accurately estimating ammonia volatilization. Nitrogen loss mechanisms in animal manure systems require further characterization to be fully understood. Groot Koerkamp and Elzing (1996) maintain the need for understanding the influential parameters and reactions in degrading litter that lead to ammonia volatilization.

The objectives of this research were twofold: 1) to determine the magnitude of irregularity among litter parameters by intensive sampling and 2) to investigate the spatial variability of litter nutrients and litter gas flux within commercial broiler houses, hypothesizing those trends in variability could enhance understanding of litter variability and possibly identify housing/management strategies for reducing ammonia emissions.

*Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U. S. Department of Agriculture.

Materials and Methods

Twenty-four hours after chicks were placed in two solid sidewall commercial broiler houses (sampling day 2), litter samples were taken, chilled and transported to the laboratory for further analyses. Gas flux was estimated, at the same locations as litter sampling, using inverted plastic chambers and a photoacoustic multigas analyzer (Figure 1). Routine litter management (decaking) had been performed in house one (H1) and house two (H2) prior to chick placement. In H2, a litter amendment had been added to the brood area (the half of the house from the cooling pad end to the center). Approximately 26,000 broilers were placed in each house.

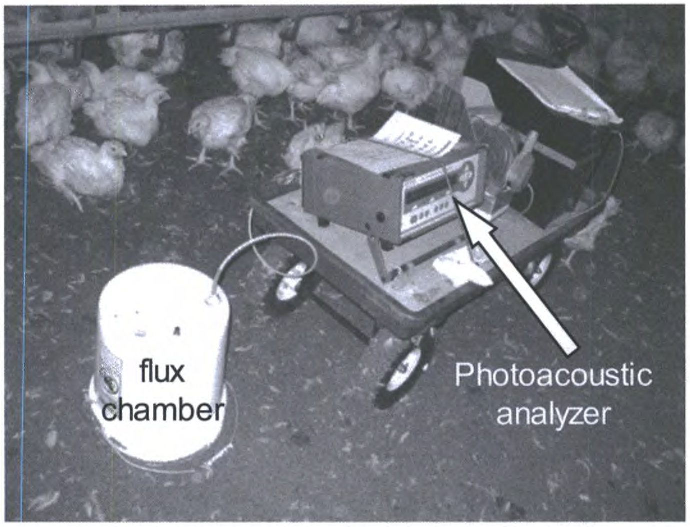


Figure 1. Gas flux chamber and photoacoustic multigas analyzer on day 45.

Pine shavings were the original bedding material; twelve flocks had been grown on the litter prior to this experiment. Near the end of the growout (day 45), grid samples for litter and gas flux were repeated. The growout conditions were during the winter in Mississippi. The houses measured 12.8 m by 146.3 m (42 ft by 480 ft) with evaporative cooling pads on the west end. Litter samples (n=36 on day 2; n=44 on day 45) were collected along the grid depicted in Figure 2. Three sampling points, 5 m apart, were placed across the house and 12 sites down the house, 12 m apart, to make up the grid. On day 45, eight additional samples were taken in a zig-zag pattern down the house to investigate litter and gas flux properties in high traffic areas where greater manure deposition might be influential. The location of the two feeder lines were approximately 1 m towards the center of the house from the outer grid samples. Litter samples were taken from the upper 10 cm at each sample location. Litter properties determined at the laboratory included moisture by loss in weight after drying 48 hours at 65 C, and pH using a litter:deionized water = 1:5. The litter was water extracted for determining ammonium and nitrate using Lachat Flow Injection Analysis.

Deriving ammonia flux from a source can include theoretical relationships or measurements of N mass balance such as models or emission factors, micrometeorological techniques or chamber methods (Arogo et al., 2003). At each sample site, a flux chamber (cylindrical with 35 cm height, 14.3 cm radius, containing a small electric fan) was inverted over the litter as the analyzer drew in the time zero gas sample. The chamber fan mixed the air within for 10 s prior to the second sample, captured at 70 s after time zero. The chamber area, elapsed time, concentration difference and the ideal gas law were used to approximate litter gas flux at each location. Litter surface temperature was measured concurrently with gas sampling.

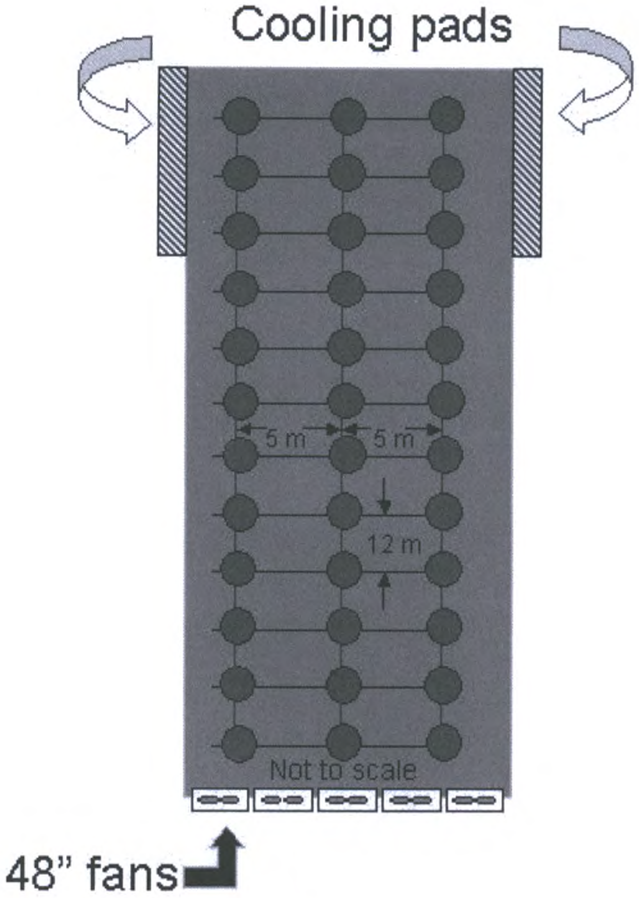


Figure 2. Grid sample layout in broiler house.

Methodology has been given elsewhere in further detail (Miles et al., 2006). Also, similar flux methods have been used in nutrition trials and for evaluation of litter amendments (Ferguson et al., 1998 a, b; Moore et al., 1997).

Variograms (contour plots) were developed using geostatistical software (Surfer 8.0) to visually survey the spatial variability among measured parameters and gas flux estimates. Without the availability of color reproduction, their use is limited. For brevity in this report, variograms are presented for ammonia flux only. Results for the intensive sampling efforts have been presented here in tabular form as means and ranges. Because the grid sampling imposes bias (samples are not random), traditional statistics were not applied to the litter and gas parameters.

Results and Discussion

The primary influences on ammonia volatilization from litter are recognized as temperature, moisture and pH (Elliot and Collins, 1982; Carr et al., 1990). These litter parameters for the two broiler houses, as well as ammonia flux and litter ammonium and nitrate, are given in Table 1. Because the chicks were in half house brood on the day 2, it is recognized that the report for average temperature is misleading. The average of the brood and non-brood areas would be more representative of what the birds experienced. The range of litter temperature was similar in H1 and H2 on day 2 at approximately 18 to 42 C. On day 45, the average litter temperature for both houses were greater than on day 2, 27.7 vs. 27.2 C. External temperatures are not provided and some herding of the birds existed while accomplishing the measurements. However, it was obvious that the larger birds insulate the litter surface towards the end of the flock which may be more influential on litter gas flux than seasonal conditions.

Table 1: Selected pooled litter gas flux, properties, and nutrients for two solid sidewall commercial broiler houses after 12 flocks on pine shavings bedding.

Bird Age (day)	Location	Litter Properties Temperature (C)	 pH	 Moisture (%)
2	H1	27.0 (18.3 to 44.2)	8.61 (8.31 to 8.85)	22.6 (13.4 to 33.0)
	H2	27.2 (18.3 to 41.4)	8.33 (6.58 to 8.90)	24.9 (12.3 to 32.1)
45	H1	27.8 (24.2 to 31.1)	8.43 (7.76 to 8.78)	29.5 (18.1 to 38.3)
	H2	27.6 (23.0 to 31.9)	8.00 (5.44 to 8.60)	36.4 (16.1 to 57.5)

Bird Age (day)	Location	Litter Gas Flux (mg m^{-2} hr^{-1}) NH_3	Litter Nutrients (mg/kg) NH_4	 NO_3
2	H1	400 (149 to 769)	3631 (2020 to 5425)	1145 (409 to 2705)
	H2	307 (0 to 1151)	5109 (2769 to13,143)	2350 (684 to 4336)
45	H1	694 (0 to 1455)	6184 (4341 to 8241)	110 (25 to 2136)
	H2	649 (0 to 1463)	7651 (3440 to 24,506)	89 (0 to 665)

Litter pH appeared to decline over the flock on average. In H1, litter pH dropped from 8.61 to 8.43. In H2, average litter pH was initially 8.3 vs. 8.0 at the end of the growout. The freshness of the feces in the sample can reduce pH, but this would not explain the decline, especially considering the numbers of samples contributing to the average. Litter pH is expected to increase with age and the number of flocks (Nahm, 2003). Used sawdust bedding has a pH between 5 and 6.5 (Elliott and Collins, 1982). The litter amendment applied to the brood area of H2 produced consistently lower pH on day 2. An area of extreme cake formation near the exhaust fans in H2 on day 45 resulted in the lowest recorded pH of the experiment, 5.44. Reece et al. (1979) demonstrated that modest ammonia volatilization occurs at pH 7 and below.

The average litter moistures in Table 1 show an increase during the flock. Individual areas ranged from very dry during brood (~13%) to very moist in the high cake areas at the end of the flock (~57%). The relationship between moisture and cake is discussed further below.

Litter ammonia flux followed a trend similar to litter moisture, increasing with bird age. On day 2, the litter treatment in H2 seemed responsible for a lesser overall flux estimate; 307 mg m^{-2} h^{-1} vs. 400 mg m^{-2} h^{-1} in H1. However, similar values for overall flux were evident by the end of the growout, 694 and 649 mg m^{-2} h^{-1}. Considering the numerous interrelated factors (i.e. diet, house management) that are house specific as well as the differences in methodology, the flux values appear reasonable compared to other chamber measurements. Brewer and Costello (1999) reported a mean ammonia flux of 208 mg m^{-2} h^{-1} after six flocks were raised on rice hulls. Baracho et al. (2001) found day 39 ammonia flux (wood chip bedding) averaged 2568 mg m^{-2} h^{-1}.

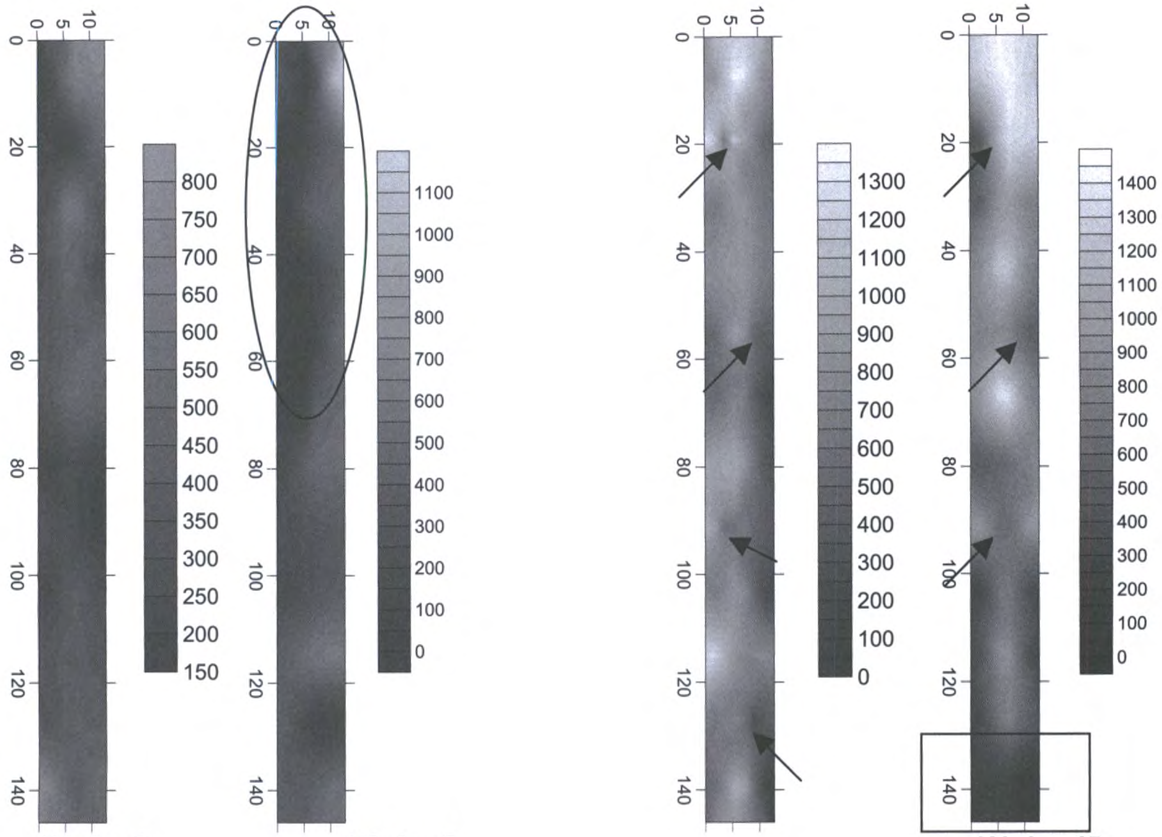
Variograms for ammonia flux over the floor area of the two houses are presented in Figure 3. The pair of plots on the left represent day 2, where the darker shading is indicative of lower ammonia flux. The oval around the brood area of H2 denotes the litter treatment area where the ammonia flux was essentially zero over approximately 45% of the area. In the brood area of H1, ammonia flux is elevated down the center of the house, which corresponds to the location of hanging brooders (gas fired heaters).

The right pair of plots represents day 45 measurements. Higher flux areas appear as lighter shading, indicating the end of the house near the cooling pads and down the center of the house have higher ammonia flux. The arrows on the day 45 variograms approximate the location of feeder and waterer (F/W) samples where ammonia flux was generally less than surrounding samples. Litter nitrate concentrations were elevated for the F/W samples. These areas were predominantly cake, but had lower moisture and pH (expected to result from the addition of dry matter from spilled feed) than the surrounding friable litter. Another area in H2, denoted by the rectangle over the fan area on day 45, was predominantly caked as well. This area had low ammonia flux, low litter pH, high litter moisture and high litter ammonium. The cake becomes anaerobic wirh high moisture which diminishes ammonia generation (Carr et al., 1990), but, as yet, the moisture boundary has not been distinguished. Additionally, the compaction of the cake from bird traffic seams to act as a physical barrier impeding ammonia volatilization, but, again, the physical effect of the cake condition has not been defined.

Litter moisture is controlled by ventilation (Gates et al., 1997) and rates are usually lower in winter to conserve heat. Increased rates are required to reasonably reduce ammonia levels within the house, which are higher than rates needed for moisture control (Xin et al., 1996). Although emissions may decrease at moisture extremes, appropriate relationships for intermediary levels have not been developed (Elliott and Collins, 1982). Large increases in aerial ammonia may occur at >30% moisture (Carr et al., 1990). Litter moisture ranging from 25-35% has been suggested as favorable for reduced odor/dust, but individual house features should be known to arrive at a precise level (Carey et al., 2004). The formation of cake within houses is currently unavoidable, and, although the diminished ammonia flux from caked surfaces may be desirable, pathogen persistence in cake is not. It is apparent that cake formation during the flock can affect the accuracy of predicting ammonia emissions.

Conclusions

During a winter flock, a static chamber method was used to capture volatilized ammonia to learn more about the surface chemistry of the litter and how litter and gas parameters change over the floor area. Litter properties and gas flux varied throughout the broiler houses. House management, feeder/waterer placement and bird activity influence litter gas flux and nutrient level. Data trends agree with established relationships for the influence of pH, moisture, and temperature on gas emissions. However, aberrations in the physical condition of the litter should be considered and quantified in future emission models. Litter amendments are the primary means for altering litter pH. They are effective, but time limited. Bird age affected litter temperature; the larger birds appeared to insulate the litter base which may somewhat negate seasonal effects on emissions. Caked areas in the house produced lower ammonia flux, but differed in moisture content based on location. Cake moisture was lower near feeders and waterers but higher near the exhaust fans. Further studies of the spatial variability are expected to lead to new best management practices that would require input from broiler managers to prevent detrimental consequences for the birds. Zone litter treatment during the flock is one example.



H1 day 2 **H2 day 2** **H1 day 45**
H2 day 45

Figure 3. Variograms of litter ammonia flux (mg m^{-2} h^{-1}) in two commercial broiler houses (H1 and H2) on days 2 and 45 of a winter growout. Feeder/waterer sample locations are denoted by arrows (→). The oval covers the brood area in H2 (day 2), indicating the litter treatment application. The rectangle over the fan area in H2 on day 45 is an area of intense cake formation.

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Volatile Organic Compound and Greenhouse Gas Emissions from Dairy Cows, Waste, and Feed

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Abstract

California is the nation's leading dairy state. Unfortunately, it is also home to two of the three worst air-sheds with respect to ozone (smog) pollution and the second largest contributor of Greenhouse Gases (GHG; e.g., methane) in the nation.

Current regulatory estimates suggest that dairy cows in central California emit smog forming, so-called volatile organic gases (VOCs), at rates higher than those from vehicles, and thus contribute significantly to the region's extreme ozone non-attainment status.

During decades of VOC studies at the University of California at Riverside and Berkeley, researchers identified biogenic sources (i.e. plants) as one of the most significant VOCs producers (e.g., for isoprenes). It is estimated that approximately 6-10 % of net primary crop production in California's main dairy region, the San Joaquin Valley, is fed to and consumed by dairy cows, which then carry out enteric fermentation leading to emission of VOCs and GHG during eructation.

The objective of the present studies was to investigate VOC and GHG emissions from dairy cows (enteric fermentation), waste, and feed, experiments were conducted using environmental chambers at UC Davis to simulate emissions under freestall cow housing conditions.

Environmentally-controlled chambers were used to simulate freestall housing conditions for a series of 15 groups of 3 cows/group (three groups each for far off and close up dry cows, low, mid, and late lactation cows). Fresh air flow was provided by forced ventilation at 1330 ft^3 min^{-1}. Food and water were provided for the cows *ad libitum*. The cows' excreta accumulated on the concrete floor until the chamber was cleaned.

Pumps pulled chamber inlet or outlet air at controlled flow rates from the appropriate vents in the air manifolds on the chamber ceiling to the analytical gas instruments.

Gas chromatography/ mass spectroscopy, proton transfer reaction mass spectroscopy, photo-acoustic spectroscopy, and laser-enhanced spectroscopy were used to measure a suite of smog forming VOCs emitted from dry and lactating dairy cows and their waste. Furthermore, GHG (methane, nitrous oxide, carbon dioxide) and ammonia were measured.

Preliminary results from our experiments suggest that a much higher percentage of the VOCs and GHG is actually produced by the cows rather than their fresh waste.

This finding may suggest that controlling these pollutants that are produced directly by the animal needs increased attention to arrive at cost effective management strategy for reducing emissions. Since this production occurs when cows digest plant matter, it is more difficult to manage than methane from manure.

While VOC emissions were considerably lower than current regulatory estimates suggest, GHG emissions were higher, which might become relevant if California starts regulating gases that contribute to global warming.

The total emissions for all measured organic carbonaceous gases (VOCs and methane) was clearly dominated by methane. When cows were present in the chambers, VOCs were less than one percent of total organic gas (TOG), which is a factor of 10 smaller than that historical and current emission estimates used by the air regulatory agencies. A significant source of VOC emissions during the present studies were from feedstuff, namely alcohol emissions from silage. However, additional research is needed to quantify silage emissions and to compare emissions from different silage types.

Furthermore, the ozone-forming-potential (OFP) of the most abundant VOCs measured in our experiment is only about 20% those of typical combustion or plant-derived VOCs. The present findings suggest that dairy cattle and their fresh waste have a smaller effect on ozone formation but a larger effect on GHG than currently assumed by air quality agencies in California.

Key Words: Dairies, Greenhouse Gas, Volatile Organic Compound

Ammonia and Trace Gas Emissions from Organic Fertilizers Amended with Gypsum

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Abstract

More than 2/3 of anthropogenic ammonia emissions (NH3) result from animal operations with most NH3 deriving from urea excreted from cattle and swine and uric acid from poultry. NH3 emissions are accompanied by emissions of nitrous oxide (N2O) and methane (CH4), trace gases with high impact on global warming and destruction of the stratospheric ozone layer. From experiments on paddy rice fields the inhibiting effect of sulfate on CH_4 emissions is known. In field trials as well negative correlations between N_2O emissions from soils and soils sulfate contents were found. From this correlations the possibility of emission reduction through sulfate was deduced. First experiments about the general influence of gypsum (calcium sulfate) on both NH3 and trace gas emissions from animal wastes were carried out. Emissions of these gases were measured in a lab experiment while broiler manure and liquid swine manure were stored in open vessels. Gas fluxes were measured daily with a multigas monitor. Contents of dry matter, NH_4-N, and total N were determined from the animal wastes.

After 10 days of storage cumulative emissions from liquid swine manure reached 2,350 g NH_3, 0.56 g N_2O, and 5,680 g CH_4 per kg dry matter at maximum. Reduction of N_2O and CH_4 emissions by addition of gypsum was as high as 62 % and 26 %, respectively.

From poultry manure cumulative fluxes after 10 days of storage were 487 g NH_3, 25 g N_2O, and 8,593 g CH_4 per kg dry matter at maximum. Reduction of NH_3 and CH_4 emissions was as high as 7 % both.

Emissions of N_2O and CH_4 were up to 45times higher from poultry manure than from liquid swine manure while emission of NH_3 was more than 5times higher from liquid swine manure than from poultry manure (emissions per kg dry matter).

Effects in reduction are related to the dry matter contents of the investigated materials and the dry matter dependent existence of anaerobic microsites. High reduction effects in liquid swine manure which derive from addition of gypsum may be caused by anaerobic CH4 oxidation and its connection to denitrifying processes including N_2O formation and anaerobic NH_3 oxidation. Above all, it seems to be possible to reduce NH3 and trace gas emissions from animal wastes by addition of gypsum.

Introduction

Because of the clean air acts SO_2 emissions in western Europe are decreased drastically (Dämmgen et al., 1998). Thus macroscopic sulfur (S) has become a major limiting factor for plant production in industrialized as well as remote rural areas (Schnug & Haneklaus, 1998). On the other hand recent research has shown that sulfate reduces CH4 formation because of substrat competition between sulfate reducing microorganisms and Methanogens (Corton et al., 2000; Wassmann et al., 2000; Gauci et al., 2004). Furthermore sulfate as part of sulfuric acid is used in waste air treatment systems to reduce NH3 emissions from animal housing (Hahne & Vorlop, 2001). Model (2004) has found a positive relation between nitrate sulfate ratio in soils and nitrous oxide emissions from organic farming systems. That means that the more sulfate in relation to nitrate is found the less N_2O is emitted.

With respect to all this positive impacts of sulfate in reducing gaseous emissions lab experiments were carried out to investigate the general influence of gypsum (calcium sulfate) on both NH3 and trace gas emissions from animal wastes. Gypsum is one of a few mineral fertilizers allowed to use in organic farming.

Methods

Experiment I - Material

Broiler manure (feces-litter-mixture) was taken from a broiler house with 29,000 animals at all at day 35 of fattening. 8 vessels with a volume of 65 liter each were filled with 2 kg of this mixture respectively. In four of them gypsum (50 g per kg mixture in one rate) was added. This two variants were examined over a period of two weeks.

Experiment II - Material

Liquid manure from fattening pigs was taken from a housing system with 8,000 animals at all. Two variants were examined with 100 Liter each over a period of four weeks. Gypsum was added with 12 g per kg liquid manure in three rates one day before starting the measurements and at day 8 and 22 of the investigation period.

Trace Gas Measurement

Broiler manure and liquid swine manure, respectively, were stored in open vessels which were closed only for gas measurement. Gas measurement was done with a multigas monitor three times per week at minimum. Cumulative gas fluxes were calculated in relation to the dry matter content of the feces-litter mixture for a period of 10 days of each experiment.

Results and Discussion

Experiment I

NH_3 emission rates ranged between 3.3 and 1.6 g per kg dry matter and day in both variants. The emission from gypsum amended variant was constant lower than from control variant at least up to 11 % (Figure 1A). Cumulative fluxes after 10 days of storage were 487 g NH_3 from control variant and 452 g NH_3 per kg dry matter from gypsum amended variant, respectively (Figure 3). Thus, reduction of NH_3 emission was as high as 7 %.

CH_4 emitted on a constant high level from the first untill the last day of the investigation period (Figure 1B). Emission rates ranged between 42 g and 31 g CH_4 per kg dry matter and day with constant higher rates from control variant (up to 9.2 % per day). Constant high emission rates indicate a full microbial activity untill the last day of measurement and thus the need for a longer investigation period. Cumulative fluxes after 10 days of storage were 8,593 g CH_4 from control variant and 7,977 g CH_4 per kg dry matter from gypsum amended variant (Figure 3). At least a reduction of CH_4 emission was observed as high as 7 %, too.

In opposite to NH_3 and CH_4 emissions highest N_2O emission rates were observed at the last two days of investigation period (Figure 1C). At least N_2O emission rates ranged between 102 and 89 mg per kg dry matter and day in both variants. Constant lower emission was observed from control variant (up to 14 % per day). 10 days after storage cumulative fluxes were 22 g N_2O from control variant and 25 g N_2O per kg dry matter from gypsum amended variant (Figure 3). In this case a reduction of N_2O emission was not observed.

It's important to notice that cumulative N_2O emission was orders of magnitude lower than CH_4 and NH_3 emissions, while NH_3 emission was only one order of magnitude lower than CH_4 emission. CH_4 and NH_3 emissions were highly positively correlated ($R = 0.884$, $p < 0.000$). On the other hand both CH_4 and NH_3 emissions were negatively correlated with N_2O emission ($R = -0.424$, $p < 0.001$ and $R = -0.404$, $p < 0.001$, respectively).

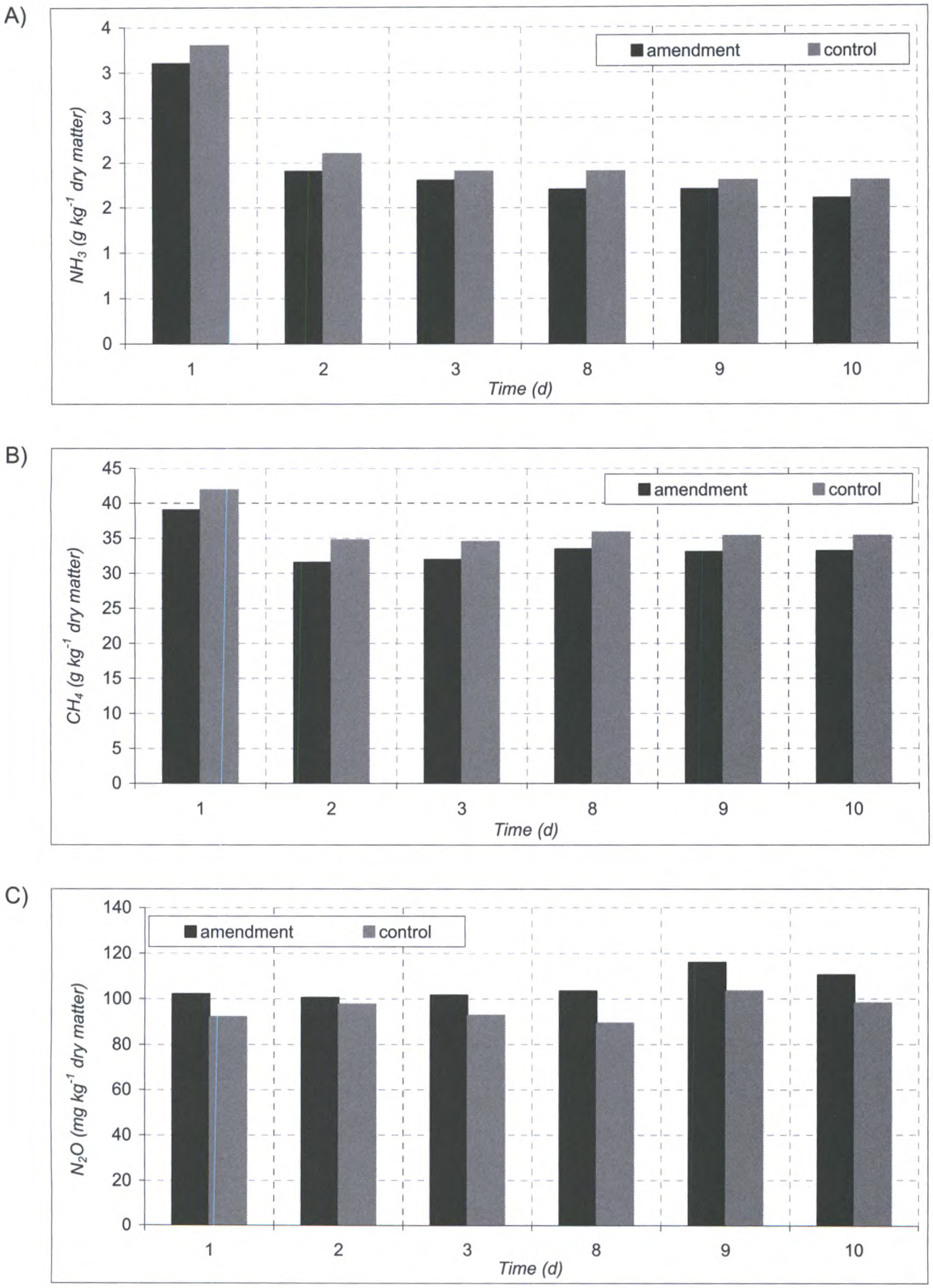

Figure 1: Gas fluxes from broiler manure

Experiment II:

With respect to results in Experiment I gas flux measurement was done over a period of four weeks now. In this period NH_3 emission rates ranged between 5.0 and 20.3 g per kg dry matter and day in both variants. Only the third rate of added gypsum led to constant lower emission rates from this variant in opposite to control variant (Figure 2A). The second rate of added gypsum induced only short term effect (day 8 in Figure 2A), and the effect of the first added rate was not measurable. So a clear reduction of NH_3 emission by addition of gypsum was not found. Hence the question arises, what is the most effective application rate and in relation to which parameters it is best calculated. Cumulative fluxes after 10 days of storage were 2.3 kg NH_3 from control variant and 2.4 kg NH_3 per kg dry matter from gypsum amended variant, respectively (Figure 3). That means that NH_3 emission from liquid swine manure was about five times higher than emission from broiler manure.

As like as with broiler manure CH_4 emission was constant lower from gypsum amended variant (up to four times at day 23, see Figure 2B). In opposite to NH_3 emission the effect of added gypsum is clearly to be seen. Each first day after addition (day 1, 9, and 23 in Figure 2B) the difference between emissions from both variants is greatest and than reduces with time. At the end of the whole measuring period the reduction of CH_4 emission by addition of gypsum was as high as 27 % (8.1 kg in opposite to 11.0 kg CH_4 per kg dry matter). After 10 days of storage cumulative fluxes reached 5.7 kg CH_4 from control variant and 4.2 kg CH_4 per kg dry matter from gypsum amended variant (Figure 3). That means that CH_4 emission from liquid swine manure was nearly two times lower than from broiler manure.

In this experiment negative N_2O emission rates were calculated. In a first step technical problems in gas measurement could be excluded. In a next step it must be investigated if N_2O uptake into the manure or N_2O consumption could take place under lab conditions. Emission rates ranged between -10.5 mg and 70.0 mg N_2O per kg dry matter in both variants. With exception of the last two days the emission from gypsum amended variant was lower than from control variant. In cases of calculated N_2O consumption this was constant higher in gypsum amended variant. At the end of the whole measuring period the reduction of N_2O emission by addition of gypsum was as high as 71 % (2.5 g in opposite to 8.7 g N_2O per kg dry matter). After 10 days of storage cumulative fluxes reached 0.56 g N_2O from control variant and –0.21 g N_2O per kg dry matter from gypsum amended variant. That means that N_2O emission from liquid swine manure was negligible in comparison with broiler manure (Figure 3).

As like as with broiler manure cumulative N_2O flux was orders of magnitude lower than CH_4 and NH_3 emissions, while CH_4 and NH_3 were emitted in the same order of magnitude. CH_4 and NH_3 emissions were negatively correlated in this experiment ($R = -0.621$, $p < 0.000$). No correlation was found between CH_4 emission and N_2O flux. On the other hand N_2O and NH_3 fluxes were slight negatively correlated ($R = -0.316$, $p < 0.001$).

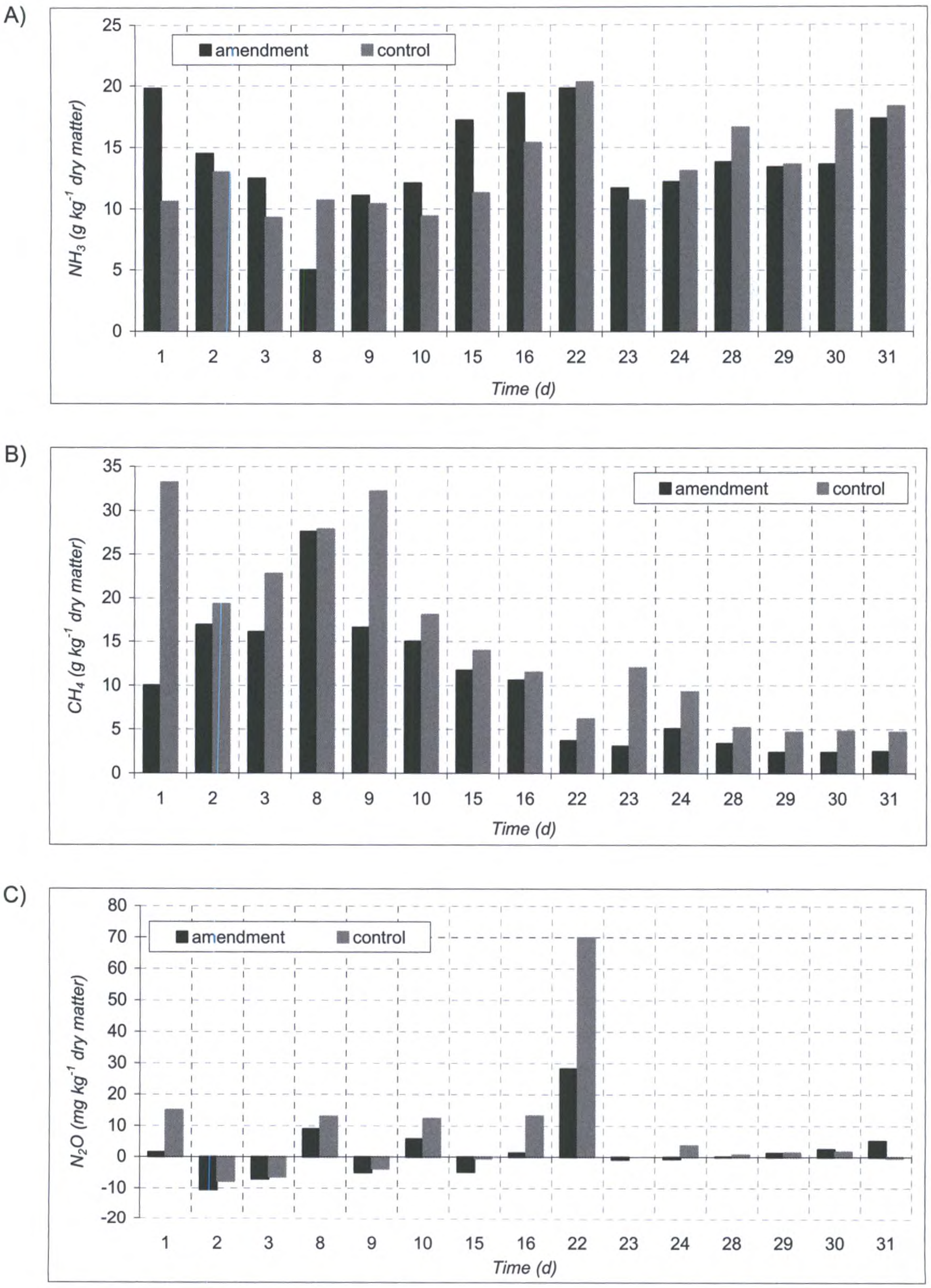

Figure 2: Gas fluxes from liquid swine manure

Comparison between both experiments:

Data from CH_4 emission measurements are in good agreement with results described by Gauci et al. (2004) and Dise & Verry (2001). Both found a reduction of methane emission in sulfate amended plots (up to 30 %). Lower CH_4 fluxes as well as lower N_2O fluxes from liquid swine manure might be caused by anaerobic CH_4 oxidation and its connection to denitrifying processes including N_2O formation. Anaerobic CH_4 oxidation was described by Nauhaus et al. (2002) in marine sediments. Model (2004) describes the possible connection between anaerobic CH_4 oxidation and N_2O formation for slurry treated soils. Because of more aerobic conditions in the broiler manure this processes might not occur with the same intensity as under anaerobic conditions in liquid swine manure. Higher NH_3 emissions from liquid swine manure are because of the higher NH_4-N content than in broiler manure (4.2 g in opposite to 2.9 g per kg manure). Independent of single results the experiments indicate the generell capability of reducing gaseous emissions from manure by addition of gypsum.

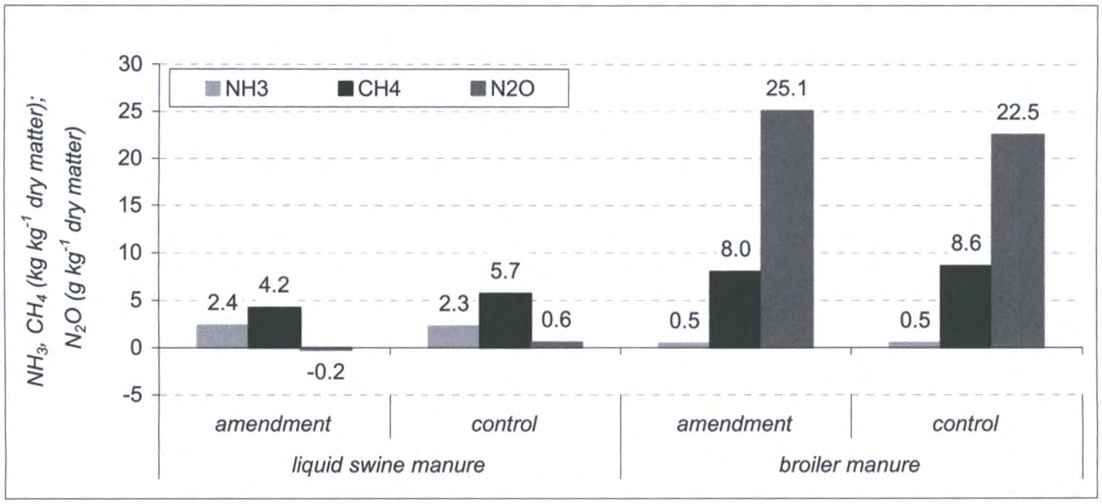

Figure 3: Cumulative gas fluxes from liquid swine manure and broiler manure 10 days after storage (take care of the different dimensions at y-axis)

Conclusions

There are already a number of investigations on mitigation strategies with most of them focussing on one gas only. They neglect the fact, that conditions reducing the emission of one trace gas might have a directly opposed effect on another (Wulf et al., 2001). By addition of gypsum it seems to be possible to reduce NH3 as well as trace gas (CH_4, N_2O) emissions from animal wastes. In further experiments it is necessary to find out optimum application rates and conditions to provide best impact of sulfate addition.

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Determination of Crop Specific Management-Related Background Flux Rates to Discriminate Fertilizer Induced Emissions

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Abstract

Nitrous oxide (N_2O) is a greenhouse gas that contributes to radiative forcing of the atmosphere. Nearly 60 % of the N_2O emitted into the atmosphere are released by natural as well as by agricultural and forest soils with 35,5 % by agricultural soils. The N_2O gas flux from agroecosystems is highly dependent on management. Most important factors are fertilizer and/or manure application. To describe the influence of fertilizing/manuring it is usual to calculate fertilizer induced emissions. In this calculation background fluxes are involved. In the literature background fluxes used to discriminate fertilizer induced N_2O emissions have been measured on plots without fertilizer application and are subtracted from emission rates measured on plots with fertilizer application. Problems of NH_3 emissions from organic fertilizers and its deposition onto adjacent unfertilized plots have been ignored, but could cause increased N_2O emissions in the unfertilized plots. Above this mineralization rates in unfertilized plots are often higher than in fertilized/manured plots. Another problem is that the crops in unfertilized plots often differ from the fertilized crops (e.g. poplar tree plots versus rape or grassland plots and grassland plots versus wheat or potato plots). In this case the plant specific N uptake as well as the plant specific influence on soil microbiology through root exudates are ignored. Because of this problems unfertilized plots should not be used for the determination of background fluxes. A statistical method was developed to determine background fluxes from the fertilized/manured plots themself. Data sets from longterm field experiments carried out near Leipzig and Potsdam were used. Background flux rates of N_2O were calculated as mean values of emission rates in the range from 0 µg to <15 µg N_2O-N m^{-2} h^{-1}. Most of them were observed in periods not influenced by any treatment (e.g. ploughing up of legumes, fertilizing/manuring). Instead of treatments they are influenced by the amount and the degradability of root and harvesting residues. For the plot near Leipzig a management-related background flux of 7,5 µg N_2O-N m^{-2} h^{-1} was calculated. The background flux of the plot near Potsdam was in the same range.

Introduction

The N_2O gas flux from agroecosystems is highly dependent on management. Most important factors are fertilizer and/or manure application. To describe the influence of fertilizing/manuring it is usual to calculate fertilizer induced emissions (Bouwman, 1996; Simojoki & Jaakkola, 2000). In this calculation background fluxes are involved. In the literature background fluxes used to discriminate fertilizer induced N_2O emissions have been measured on plots without fertilizer application and are subtracted from emission rates measured on plots with fertilizer application (Bouwman, 1996). Problems of NH_3 emissions from organic fertilizers and its deposition onto adjacent unfertilized plots have been ignored, but could cause increased N_2O emissions in the unfertilized plots (Hellebrand & Scholz, 1997; Model, 2004). Above this mineralization rates in unfertilized plots are often higher than in fertilized/manured plots (Stahr et al., 1994; Beckmann et al., 2001). Another problem is that the crops in unfertilized plots often differ from the fertilized crops (e.g. poplar tree plots versus rape or grassland plots and grassland plots versus wheat or potato plots)(Teepe, 1998; Schmädeke, 1998; Kaiser & Ruser 2000). In this case the plant specific N uptake as well as the plant specific influence on soil microbiology through root exudates are ignored.

Methods

Experimental Sites, Gas Flux Measurement

Gas fluxes of nitrous oxide, methane, and carbon dioxide were determined in long term field trials at experimental station Spröda, 35 km northeast from Leipzig over a period of three years in the crop rotation alfalfa/grass-summer wheat-rye/vetch mixture-maize and at agricultural research fields of the Leibniz-

Institute of Agricultural Engineering Potsdam-Bornim (ATB) over a period of seven years in the crop rotation rye-hemp-rye-oilseed rape-rye-triticale-rye. Sandy loam soils dominate both sites which are characterised by dry climate. Trace gas fluxes were measured with closed boxes up to five times per week. Detailed descriptions of both experimental sites and gas flux measurement methods are given in Model (2004) and Hellebrand et al. (2005).

Statistical Method for BFR Calculation

All measured emission rates were subdivided into classes with upper and lower borderlines which are shown in Table 1. In the first step the subdivision was independent from variants to get one value which characterises the background flux of the whole experimental site. Therefor a mean value was calculated from emission rates of those classes containing the most values. As an example in Table 1 the N_2O emission rates of Spröda experimental site are given as in per cent per class (values in parentheses). In the next steps the subdivision was dependent on systems, variants or single crops.

The periods influenced by treatment measures (manure application, ploughing up of legume grass) were narrowed in time when gas flux rates in the range of those determined just before starting the measure were found the first time again (for detailed description see Model, 2004).

Table 1. Categories and upper borderlines for trace gas fluxes used in determination of management related background fluxes.

Classes with upper borderlines ($\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1}$)									
<0	<5	<10	<15	<20	<30	<40	<50	<100	>=100
(4.1)	*(13.7)*	*(17.6)*	*(10.1)*	(7.5)	(12.0)	(9.7)	(3.6)	(11.1)	(10.3)

Results and Discussion

At the Spröda experimental site in 21 per cent of all measurements N_2O emission rates with more than 50 $\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1}$ were detected. 89 per cent of this emission rates were found in periods influenced by treatment measures, and about 6 per cent were found in winter time. In 33 per cent of all measurements N_2O emission rates with more than 15 μg but less than 50 $\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1}$ were detected. Half of this rates were found in periods influenced by treatment measures, too. Most N_2O emission rates (42 per cent) ranged between 0 μg and 15 $\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1}$. Only 11 per cent of this rates were found in periods influenced by treatment measures. That means that emission rates of this range mostly were found in periods without any direct influence of manure application and ploughing up of legume grass, respectively. On the other hand the influence of site specific parameters might be stronger on processes resulting in N_2O formation in this periods. Thus emission rates of this range were used to calculate management related background fluxes. This background flux was as high as 7.5 $\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1}$.

At the plot near Potsdam a management related background flux as high as 8.2 $\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1}$ was calculated. More than 50 per cent of all N_2O emission rates were between 0 μg and 15 $\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1}$ at this site. Most of them were found in periods not influenced by any treatment as well. This findings are in good agreement with results of Ruser et al. (1996). They discribe a "background level" from 0-15 $\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1}$ as well in a fertilized crop but in periods without influence of fertilizer application.

Beside nitrate availability carbon availability is important in modification of N_2O fluxes from soil (Firestone & Davidson, 1989; Aulakh et al., 1991; Benckiser, 1994). Soil respiration determined as CO_2 emission from bare soil characterises carbon availability as well as soil microbial activity (Schulz, 1986; Klimanek, 1988). The relation between carbon and nitrate is described by Umarov (1990) as $C_{org} + NO_3 \rightarrow (CH_2O)_n + CO_2 + N_2O$. Hence it is not surprising that strong correlations between N_2O and CO_2 emissions were found in a few investigations (Flessa & Beese, 1995; Parsons et al., 1991; Simojoki & Jaakkola, 2000).

Management related background fluxes of N_2O and CO_2 depending on single crops are given in Table 2 for Spröda experimental site (for calculation of CO_2 background fluxes see Model, 2004). Furthermore in this table values are given for amounts of root residues, detected from Klimanek (1997) in long term field trials at different experimental sites. Both N_2O and CO_2 background fluxes could be set in a descending order as summer wheat > maize >= alfalfa grass > rye/vetch mix. The same descending order is to be found for the mineralizable root residues available from the previous crop. That means that highest amounts of mineralizable root residues are left in the soil by alfalfa grass and might be decomposed in the period of growing summer wheat. In that time where highest amounts of mineralizable root residues were available highest background fluxes of both N_2O and CO_2 were found. On the other hand lowest background fluxes of both N_2O and CO_2 were found in the same period in which lowest amounts of mineralizable root residues were available. This findings agree with results of Rosswall et al. (1989), Fauci & Dick (1994), and Singh & van Cleemput (1997). All of them found positive correlations between N_2O as well as CO_2 emissions and the amount of root residues left in the soil.

Table 2: Influence of crop rotation on trace gas fluxes at Spröda experimental site

	alfalfa/grass	summer wheat	rye/vetch-mix	maize
BF N_2O	0.7	0.8	0.5	0.7
BF CO_2	6.6	8.1	6.4	6.5
RR	10.8	1.4	2.4	2.4

BF N_2O and CO_2 = Management-related background flux rate (kg N_2O-N ha^{-1} $year^{-1}$; t CO_2-C ha^{-1} $year^{-1}$); RR = mineralizable root residues (mean values t dry matter per ha, Klimanek, 1997)

Conclusions

Because of the problems mentioned above unfertilized plots should not be used for the determination of background fluxes. With the described method a good measure is given to determine management related background fluxes. This background fluxes provide useful emission factors to compare sites or cropping systems differing in management parameters and to establish site and crop specific emission inventories. Furthermore they allow quantification of the influence of crop rotation on trace gas fluxes.

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A Scenario of Agricultural Air Emissions: Bangladesh Perspective

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Abstract

Bangladesh is situated in the South Asia a densely populated more than 150 million people live in this country. About 85% people of this country live on agriculture and about 35% of total GDP comes from this sector. Only 20-25% people of total live in urban area they used Natural gas for cooking. But rest of the people live in village or remote area and they burn Agricultural by product which mainly come from crops and animals like, Straw, Rice husk, Wheat straw, Jute plant, Corn husk, maze plant, wood and Cow dung for their cooking purpose. As a result, a huge amount of carbon dioxide (CO_2), sulphur dioxide (SO_2), Hydrocarbon (HC) are emitting in the air continuously. That why air is being polluting every where specially in the rural area and this amount is also increasing day by day due to increase of population. Consequently, Most of house wife are effected such type of diseases i.e. Asthma, Cough, Eye irritation, Headache, Skin diseases, and some times severe carcinogenic. Same phenomena also are occurred for the children as well. Besides, agricultural operations, those that raise animals and grow crops, can generate emissions of gases, particulate matter, and chemical compounds. For example, animals confined to a barn or area (rather than field grazing), produce large amounts of manure. Manure emits various gases, particularly ammonia into the air. This ammonia can be emitted from the animal houses, manure storage areas, or from the land after the manure is applied. In crop production, the misapplication of fertilizers, herbicides, and pesticides can potentially result in aerial drift of these materials.

Agricultural practices from land cultivating, weeding, fertilizing and crop harvesting in every case several type of agricultural machineries are used and that pollutes air pollution. There is another source of air pollution in rural area. i.e. people burn a lot of straw during the morning and some time at night for protection themselves from cold in winter period (normally December to March). So necessary step should be taken immediately to protect the people as well as environment of the country especially for air pollution.

Key words: Rural areas, Pollutants, diseases, manure, Agricultural machineries

Introduction

Bangladesh is a riverine country with a land area of 147570 square kilometers (almost equal to the U.S state of Wisconsin). In this small, flood and cyclone –prone area, over 150 million people live at a per capita income level of approximately $US 344. The current population growth rate is 1.7 %, the real GDP growth rate in the year 2004 was almost 5.5%. By 2020 Bangladesh is expected to have about 200 million inhabitants, many of whom will remain under the poverty limit. The economy of Bangladesh depends on agriculture. About 84 % of total population lives in the rural area and is directly or indirectly engaged in a wide range of agricultural activities.

In Bangladesh, almost 17.83 million households are in the rural area, among them approximate 11.8 millions have the farm household and the rest of them are not related to the agricultures. In this country, there are about 17.77 million of acres of cultivated land where half of the cultivated area are irrigated. There are also a significant amount of livestock in Bangladesh and from these live stock contribute a huge amount of manure which is very important for increase the fertility of the land as well increase the organic matter of the soil but from these livestock source methane may release in to the environment and this has a great contribution to increase the green house gases in atmosphere.

Sources of Agricultural Air Emissions

Fires are the major source of air pollution and can lead to severe problems if the smoke is inhaled for a period of time. These fires can either be forest fires, oil fires, burning of dried leaves in the backyard or as in the case of rural areas, large-scale burning of agricultural waste. Other sources include industries and power plants located in these areas. Some sources of air pollution are described briefly in the below:

1) Direct Sources

a) In Bangladesh, generally bullock/buffaloes driven ploughs are used for cultivating land. But nowadays, due to less payment (approx. $1.5 for 0-12 hrs) of agricultural labor crisis is increasing in rural areas that are why agricultural machineries are more familiar to cultivators which are rapidly shifting to them. Another reason for this dramatic change may be that the use of machinery is more efficient in terms of time and budget. These are the reasons that agricultural machineries like power tillers, tractors, seed drill machines, weeding equipment, combine harvester are using widely. All these machines are driven by diesel. As a result, CO, HC, NOx, Sox, PM are emitted in the air.

b) Another important source of air pollution in the rural area of Bangladesh is rural industrialization. In rice mills, for example, rice husk is widely used for boiling rice and CO, CO_2 and SPM are emitted in the atmosphere and polluting the air.

c) Livestock farming is also responsible for air pollution. From animal urine and cow dung ammonia, hydrogen sulphide and other toxics gases mixed with air. Besides manmade methane which released from the bowels of ruminating farm animals and their manure comes from the agriculture sources. Agriculture is also the main source of artificial emissions of nitrous oxide which is caused by the soil bacteria transforming nitrogen from fertilizer and manure into nitrous oxide.

d) Now a day's small scale biomass plant is going to familiar in the rural area to meet up their electricity demand where a huge amount of cowdung is using for this purpose. Consequently, a lot of methane is produced during these activities and thus contribute major effects of air pollution and also increase the green house gases in the atmosphere.

e) During cultivation of land soils are breakdown thus releases carbon dioxide into the atmosphere. Similarly fertilizer and manure management practices in the field may emit nitrous oxide that is an important greenhouse gases. Greenhouse gases methane is also released to the atmosphere during the storage and the application of livestock manure in the field.

f) During cultivation of dry land dust particle dissimilates in the air thus have great negative impacts of health because airbone particulates directly penetrate into the lungs.

g) When pesticides are applied in the field some times it may responsible for pollutes air because pesticide droplets are drift onto the adjoining areas during unrest weather conditions.

2) Indirect Sources

a) In Bangladesh people in the rural areas burn agricultural residues, twigs, rice husks, wood, wooden dust, leaves, jute sticks, dried cow dung, and sometimes cow dung stick (jute stick inside surrounded by cow dung and then dried in the sun). These sticks are usually burned for cooking purposes. By burning these types of agricultural materials Suspended Particulate Matter (SPM), Carbon Monoxide (CO), and Volatile Organic Compounds (VOC) are emitted in the air. As a result, people, particularly women and children, suffer various complex diseases. In general, people in the rural areas burn agricultural residues, leaves, rice husk etc material outside their kitchens during the winter season (late October to March) . The rest of the year, they do it inside their kitchens.

b) During the morning time in winter season, it is a common practice in the rural area to make fire with straws and dried leaves and shake their hands and legs by sitting around the fire to protect them from cold. From these fires a significant amount of pollutants like particulate matter, carbon monoxide, nitrogen oxides, and VOC′s are emitted. Consequently, people suffer of complex diseases. This nitrogen oxide contributes to the production of green houses gases.

Picture 1: Scenario of heating during the winter in rural areas.

Impact of Air Pollution on Health

Air pollution is the major environmental health problem affecting the developing countries especially for those lives in the rural areas. The effect of air pollution on health is very complex due to their availability of different sources and their individual effects vary from one to other. In fact, in the developing countries the significant amount of air pollution exposures occurs in the indoor and some times outdoor in the rural areas. Air pollutants that are inhaled have serious impact on human health affecting the lungs and the respiratory system; they are also taken up by the blood and pumped all round the body. These pollutants are also deposited on soil, plants and in the water further contributing to human exposure.

Particularly, indoor air pollution in rural area can be hazardous to health as it is released in close proximity to people. It is stated that a pollutant released indoors is many times more likely to reach the lungs than it released ambient air. In the developing countries a large portion of the population is dependent on biomass for their energy requirements. These include wood, leaves, twigs, dried cow dung stick, rice husk, agricultural residues, and animal waste etc. Open fires used for cooking and heating are commonly found in the household both in the rural and the urban areas. The stove is often at floor level, adding to the risk of accident and the hygiene factor. In addition, they are often not fitted with a chimney to remove the pollutants. In such households the children and women are most likely to be affected, as they are the group that spends more time indoors. The main pollutants in this environment are the Suspended Particulate Matter (SPM). In fact, death due to indoor air pollution, mainly particulate matters, in the rural areas of the sub content of Asia is one of the highest in the world. Many of the deaths are due to acute respiratory infections in children; others are due to cardiovascular diseases, lung cancer, and chronic respiratory diseases in adults. If emissions are high and ventilation is poor, household use of coal and biomass can severely affect the indoor air quality.

Pollutant emissions per feast are also very high compared to those of other fuels. Household use of kerosene stove is a common practice in the developing countries. They are particularly damaging as they burn inefficiently and emit considerable quantities of air pollutants. If emissions are high and ventilation is poor, then the exposure levels to the gases emitted are much higher. The most harmful of the gases and agents that are emitted are particulate matter, carbon dioxide, polycyclic organic matter, and formaldehyde.

Health Impact of Specific Air Pollutants

Previously it is described that there is a lot source of agricultural air pollution in Bangladesh. From these source different types pollutants may be exposed in the environment which has direct or indirect health effect on human being. In the below, some possible source are described. Some of these gases can seriously and adversely affect the health of the population and should be given due attention by the concerned authority. The gases mentioned below closely related to agricultural sources are mainly ambient air pollutants but some of them can occur in indoor depending on their generation and circumstances.

Tobacco smoking: Tobacco smoking is a common practice for the person of rural area in Bangladesh. Everyday specially when they works in the field they take tobacco and often they smoke cigarette(locally called *Biri*).Tobacco smoke generates a wide range of harmful chemicals and is a major cause of sick health, as it is known to cause cancer, not only to the smoker but affecting passive smokers too. It is well-known that smoking affects the passive smoker (the person who is in the vicinity of a smoker and is not himself/herself a smoker) ranging from burning sensation in the eyes or nose, and throat irritation, cancer, bronchitis, severe asthma and a decrease in lung function.

Biological pollutants: comes from pollen plants, mite, hair from pets, fungi, parasites and some bacteria. These are mostly allergens that can cause asthma, cough, hay fever and other allergic diseases.

Volatile organic compounds (VOC): Volatile compounds can cause irritation of the eye, nose and throat. In severe cases there may be headaches, nausea, and loss of coordination. In the longer run, some of them are suspected to cause damage to the liver and other parts of the body.

Formaldehyde (HOCH): is a gas that comes mainly carpets, particle boards and insulation foam. it causes irritation to the eyes, nose and may cause allergies in some people.

Lead (Pb): Prolonged exposure can cause damage to the nervous system, digestive problems and in some cases cause cancer. It is especially hazardous to small children.

Radon (Rn): A radioactive gas that can accumulate inside the house, it originates from the rocks and soil under the house and its level is dominated by the outdoor air and also to some extent the other gases being emitted indoors. it is confined inside the house causing harm to the dwellers. Exposure to this gas increases the risk of lung cancer.

Ozone (O_3): Exposure to this gas makes our eyes itch, burn, and water and it has also been associated with increase in respiratory disorders such as asthma. It lowers our resistance to colds and pneumonia.

Oxides of nitrogen (NO_x): This gas can make children susceptible to respiratory diseases in the winters.

Carbon monoxide (CO): Carbon monoxide combines with hemoglobin to lessen the amount of oxygen that enters our blood through our lungs. The binding with other proteins causes changes in the function of the affected organs such as the brain and the cardiovascular system, and also the developing fetus. It can impair our concentration, slow our reflexes, and make us confused and sleepy.

Sulphur dioxide (SO_2): Sulphur dioxide in the air is caused due to the rise in combustion of fossil fuels. It can oxidize and form sulphuric acid mist. SO_2 in the air leads to diseases of the lung and other lung disorders such as wheezing and shortness of breath. Long-term effects are more difficult to ascertain as SO_2 exposure is often combined with that of SPM.

Suspended Particulate Matter (SPM): Suspended matter consists of dust, fumes, smog, mist and smoke. The main chemical component of SPM that is of major concern is lead, others being nickel, arsenic, and those present in diesel exhaust. When inhaled these particles, lodge in lung tissues and cause lung damage and respiratory problems. The importance of SPM as a major pollutant needs special emphasis as i) it affects more people globally than any other pollutant on a continuing basis; ii) there is more monitoring data available on this than any other pollutant; and iii) more epidemiological evidence are available on the exposure to this particle than to any other pollutant.

Legal frame

In September, 2005 government of Bangladesh has promulgated the ambient air quality standards for the country but regarding to agricultural air emissions any guideline or standards not yet established.

Conclusions

As a developing country any research project regarding agricultural air emissions has not been executed yet by the government, non-governmental organizations or donor agencies. Thus a scenario for agricultural emissions has not been elaborated yet. More investment and more research would be needed in near future to establish the current situation of agricultural air emissions in Bangladesh.

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Twisha Lahiri and Manas Ranjan Ray,Health impact of biomass fuel use in rural India, Chittaranjan National Cancer Institute, Kolkata, India.

The Relationship Between Agriculture and Atmospheric Chemistry: A Historical Perspective

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Abstract

This paper will present an overview related to changing aspects concerning air composition and agriculture within the last 150 years and near future, which are twofold: first inspiring atmospheric chemistry research and now becoming a dominating controller of atmospheric chemistry. The discovery of the main constituents of our atmosphere (nitrogen and oxygen) was in relation with the beginning understanding of combustion processes around 1790. However, already before it has been found (Mayow, Hales, Senebier) that air contains a substance (CO_2) which is essential for plant growth. Soon after discovering of oxygen (Priestley, Scheele, Cavendish, Lavoisier) it was seen that plants "restore" bad air. Soon later Ingenhousz and Saussure found that plants take up for growing not only water from soil but among carbon still other compounds from air. Boussingault first showed that nitrogen is incorporated from the atmosphere. Liebig, who is regarded to be the founder of modern agricultural chemistry, pointed out without doing experiments that this compound is ammonia. However, already a hundred years before (1733), Woodward proposed fertilizing with minerals. The early idea that plant growth is linked with atmospheric matter exchange indeed stimulated research in atmospheric chemical composition. Ammonium has been found in rain water around 1850 and even in air but not until beginning of 20th century analysed in its gaseous form. According to investigations by Robert Angus Smith, the atmospheric NH_3 concentration in and around cities must be several times larger in that time than today, probably due to decomposition of biogenic waste and still missing sanitary conditions like canalisation. The demand for increasing agriculture yield resulted in mineral fertilizing. The consequence, however, an interruption of a balanced biosphere-atmosphere budget, has been recognized only in the 2nd half of 20th century. Now agricultural emissions became first into interest of buffering acid rain (but possibly acidifying soils), later into an overloading the nitrogen cycle (euthrofication) and finally into the climate change issue (greenhouse effect). Nowadays and in future, emissions from agriculture will play a dominant role in atmospheric chemistry. With decreasing industrial emissions (e.g. SO_2, NO_X, VOC) agricultural emissions will play an increasing role in future atmospheric chemistry: ozone formation from CH_4, acidity budget from NH_3, particulate matter from soil dust. Based on own monitoring results, these topics will be illustrated.

Estimating Nitrogen Loss from Livestock and Poultry Manure Using Nitrogen to Phosphorus Ratio

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Abstract

Excessive loads of some volatile forms of N (e.g. NH_3-N, N_2O) may have negative effect on the environment and public health. Animal production systems appear to be a large source of NH_3-N. This study estimated N volatilization based on the nitrogen to phosphorus ratio, extrapolated from a dataset of manure analyzed in laboratories located in Minnesota, Pennsylvania and Wisconsin. Animal categories evaluated included broilers, dairy cows, finishing swine, and laying hens. Annual N losses were 0.21 Tg, 0.42 Tg, 0.51 Tg, and 0.60 Tg for laying hens, milking cows, finishing swine, and broilers, respectively. These figures are likely to represent N lost from animal housing and manure storage only, i.e. field losses were not included. Nonetheless, estimated annual N losses were near or well above NH_3-N emission factors published in EPA (2004).

Introduction

Livestock and poultry production systems are believed to be responsible for most anthropogenic ammonia volatilized to the atmosphere. High contents of readily hydrolysable urea or uric acid in excreta rapidly yield an abundance of ammonia in most animal production systems. Subsequent degradation of organic nitrogen compounds to ammonia results in uninterrupted, imminent potential for volatilization. Thus, nitrogen release may begin immediately after excretion and continue through every stage of manure management (housing, storage, and field application). Most nitrogen volatilizes primarily as ammonia from housing facilities, since limiting conditions for denitrification prevail in early stages of manure management.

There is noticeable scarcity of scientifically sound estimates of ammonia emission (NRC, 2003). Also, ammonia emissions vary widely depending on animal and ambient factors. Methods of measurement of N losses include direct measurements or indirect estimates. Direct measurements of ammonia in the atmosphere are costly and highly specialized. An indirect methodology can use P as a marker in manure managed within confinement areas because it remains in solid phase under ambient conditions. Thus, the objective of this study was to estimate volatile N loss from confined areas of livestock and poultry production systems using the nitrogen to phosphorus ratio (N:P).

Materials and Methods

Nutrient excretion was calculated by mass balance as the amount ingested minus the amount in products (egg, meat and milk), according to Van Horn et al. (1994). The dataset of manure nutrient content comprised manure analyzed in laboratories located in Minnesota, Pennsylvania, and Wisconsin. Dated analyses ranged from 1998 until 2002. Records included analyses of manure that originated from dairy cows (n = 813), finishing swine (n = 180), laying hens (n = 124), and broilers (n = 58). Samples origin was not known but it is assumed that sampling occurred as storage facilities were being emptied, before manure spreading. Volatilized N/day per head was estimated according to Moreira and Satter (2006). Nitrogen volatilization estimated in this study by the N:P approach does not differentiate among volatile forms of N. Therefore, estimated N losses should be considered a potential ceiling for ammonia volatilization. Animal numbers from USDA National Agricultural Statistics Service 2002 Census (USDA-NASS, 2005) were used to obtain N volatilization extrapolated for the entire U.S.

Results and Discussion

Given the source of manure analyses, N:P estimates are likely to represent N volatilization losses occurring from excretion until manure samples were collected. That occurred most probably while manure storage facilities were emptied and immediately before manure was spread onto fields. Farmers often send manure samples to be analyzed in order to adjust a fertilization program to appropriately supplement crops demands. Estimated N loss per head (Table 1) was highest with dairy cow manure (127 g cow^{-1} day^{-1}) and lowest from broiler litter (1.65 g $bird^{-1}$ day^{-1}), but total animal numbers offset the disproportions among animal categories. Annual N losses extrapolated from the dataset were 0.21 Tg, 0.42 Tg, 0.51 Tg, and 0.60 Tg for laying hens, milking cows, finishing swine, and broilers, respectively. It is important to note that N:P estimates did not consider potential losses occurring after manure application to the fields while EPA NH_3-N emission factors include the entire animal production system (housing, storage and manure application). Thus, figures shown in the Table 1 indicated NH_3-N emission factors (EPA, 2004) were much lower than N:P estimated N losses for swine and poultry but not dairy cows.

There should be little opportunity for denitrification within animal housing, where most N should be lost as NH_3-N. A larger proportion of N loss appears to originate from housing facilities in dairy production systems (Moreira and Satter, 2006; Moreira and Satter, 2005). There is evidence that denitrification (43% of N lost) may occur with highly diluted swine manure releasing N_2 from lagoons (Harper et al., 2004). Nonetheless, it is still unknown whether denitrification occurs at similar rates from less diluted dairy manure in storage facilities. A near mach between EPA and N:P estimated figures was possibly because most N is lost as NH_3-N from dairy manure. The larger proportions of N_2 may have accounted for the large disparities found for finishing swine and poultry.

Conclusion

This study showed that annual N losses were near or well above NH_3-N emission factors published in EPA (2004). The N:P can be used as an alternative to the mass balance approach whenever manure is contained within the facilities but weighing is impossible or impractical. The N:P technique can be used as a screening method to rank manure management practices according to their potential for N conservation.

Acknowledgement

We are thankful to Ann Wolf (PSU Analyses Lab), John B. Peters (Marshfield Laboratories), and Christine Henderson (Stearns County DHIA Lab) for making available the datasets for our analysis.

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Table 1. Comparison between N volatilization from manure of livestock and poultry, estimated by the N to P ratio or according to EPA (2004).

Species	DAIRY COWS	FINISHING SWINE	LAYING HENS	BROILERS
Estimated N:P in excreta	5.62	8.22	3.72	7.48
Manure analyses				
Number of analysis	813	180	124	58
N:P manure	4.42	3.74	1.57	4.24
USDA-NASS (2002 Census)				
Number of animals	9.11×10^{6}	5.35×10^{7}	3.37×10^{8}	9.97×10^{8}
N:P estimates				
N loss (%)[1]	21.3	54.5	57.9	43.3
N loss (g head^{-1} day^{-1})[2]	127	26.3	1.67	1.65
U.S. N volatilized (Tg year^{-1})[3]	0.423	0.514	0.205	0.599
			0.804[4]	
EPA estimates				
NH_3-N volatilized (Tg year^{-1})	0.460	0.354	0.547[4]	
Difference between estimates[5]	92.1	145	147	

[1] [1 – (N:Pman ÷ N:Pexc)] x 100, where subscript "man" is manure and "exc" is excreta.

[2] [1 – (N:Pman ÷ N:Pexc)] x Nexc, where subscript "man" is manure and "exc" is excreta.

[3] US N volatilized: estimation extrapolated from manure analyzed in laboratories located in Minnesota, Wisconsin, and Pennsylvania.

[4] Sum of N volatilization from poultry manure (laying hens plus broilers).

[5] Percent of EPA (2004).

Seasonal and Spatial Variations Of Ammonia Emissions from an Open-Lot Dairy Operation

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Abstract

There is a need for a robust and accurate technique to measure ammonia (NH_3) emissions from animal feeding operations (AFOs) to obtain reliable emissions data and to develop abatement strategies. Two consecutive seasonal studies were conducted and ammonia emission rates (ERs) were estimated from an open-lot dairy in central Texas. Data including NH_3 concentrations were collected and ammonia emission fluxes (EFl) and ERs were calculated for the open-lot dairy in summer and winter of 2005.

A protocol using flux chambers was used to determine these NH_3 emissions from the open-lot dairy. Ammonia concentration measurements were made using chemiluminescence-based analyzers. The ground level area sources (GLAS) including open lots (cows on earthen corrals), separated solids, primary and secondary lagoons and milking parlors were sampled to estimate NH_3 emissions. Preliminary assessment of summer and winter data indicated that overall NH_3 emission rates were 41.9 ±3.2 $kg.day^{-1}$ for the summer and 18.6 ±3.1 $kg.day^{-1}$ for the winter season. The estimated emission rate for winter was approximately 45% lower than summer emission rates. Lagoons (62%) in summer and open-lot corrals (89%) in winter were the highest contributors to NH3 emission for the open-lot dairy.

The difference between the overall emission rates from each season was due to ambient and source temperature variations, and loading rates of manure on GLAS. Higher NH_3 ERs were estimated in summer time as compared to the winter time in the open-lot dairy. There was spatial variation of NH_3 emission from the open lot earthen corrals due to variable animal density within feeding, shaded and dry areas of the open lot. This spatial variability was attributed to dispirit manure loading within these areas.

Introduction

In both Europe and United States, the largest sources of ammonia emission are livestock and poultry operations and they account for an estimated 70-90% of total emissions. Cattle including dairy cows are the largest of animal sources contributing to NH_3 emissions. Atmospheric NH_3 is considered to be a precursor to $PM_{2.5,}$ one of the 6 USEPA criteria air pollutants. It is anticipated that NH_3 emissions from animal feeding operations (AFOs) in the US maybe be regulated in the near future.

Recommendations for future NH_3 research from AFOs, including measurement techniques to establish emission factors will be necessary to develop mass balance-based models. Development of emission factors using an isolated flux chamber (FC) method will bring new insights and confidence on determining science-based NH_3 emission factor from livestock and poultry. Information on seasonal NH_3 emissions variations at ground level area sources (GLAS) from dairy operations will assist with evaluation and selection of best management practices to control and abate such emissions.

The isolated flux chamber (FC) is one of the direct measuring techniques for surface gas emissions such as NH_3. The USEPA has published a protocol using this method for GLAS emissions (Gholson et al., 1989). The technology is also applicable to liquid surfaces.

In our study, a flux chamber protocol was used to determine NH_3 emission rates from different ground level area sources in an open-lot dairy.

Two open-lots were randomly selected to represent the entire lot area. In addition, GLAS including primary and secondary lagoons, milking parlor facility and separated solids were sampled for NH_3 emissions during summer and winter conditions. NH_3 emission rates were calculated using real time NH_3 concentration and flux data.

Results of NH_3 emission from open-lot dairy are presented. Discussion includes seasonal effects and spatial effects on NH_3 emissions from GLAS at the open-lot dairy.

Materials and Methods

An open-lot dairy (Fig. 1) in central Texas was selected to estimate NH_3 emissions using a USEPA approved flux chamber measurement protocol. A description of the site is given below.

Open-lot Dairy

Approximately 2000 lactating cows were housed at the open-lot dairy during this study in the summer and winter of 2005, respectively. This dairy included 12 earthen corrals which were centralized feeding and watering areas and free standing shelters for relief from severe weather conditions. Each corral was an un-paved, confined area with access to feed bunkers and water tanks. Accumulated manure in these lots was removed by scraping using tractor mounted blades once a day. The scraped manure was stockpiled on-site between lagoons and the corrals.

There were two lagoon cells (lagoon 1 and lagoon 2) for storage and treatment of liquid manure at this dairy. Lagoon 1 received waste water from the milking parlor and runoff from corrals. Lagoon 2 was used to store effluent from lagoon 1 and to irrigate crop and pasture land.

Figure 1. Sampled Open-lot Dairy.

Isolation Flux Chamber Sampling Protocol

Real-time samples from free-stall and open-lot dairy were collected continuously using isolation flux chamber method to determine the emission rates of NH_3 from different GLAS. Isolation flux chambers have been used to measure emission fluxes of volatile organic compounds (VOCs) and inorganic gaseous pollutants from a wide variety of sources (Eklund, 1992). The design of the flux chamber includes an acrylic hemispherical top (dome) and a stainless steel cylindrical skirt. Odotech Incorporated supplied the hemispherical top for use in this research (Odotech Inc. Montreal, Canada). Mukhtar et al. (2003) have described the flux chamber used in this study.

Measurement of Ammonia Concentrations

On-site measurements for these studies were conducted by using a mobile laboratory. The mobile laboratory included NH_3 analyzers, air flow mixing devices, a multiplexer system including mass flow controllers, a zero air generator, gas cylinders and power generators for electricity.

A chemiluminescence analyzer (Model 17C, Thermo Environmental Instruments, TEI, Massachusetts.) was used to measure NH_3 for real time and continuous sampling.

Additional measurement details were provided by Mukhtar et al. (2003), Mutlu et al. (2004), Boriack et al. (2004a), (2004b) and Capareda et al. (2005).

Ammonia Flux and Emission Rate Calculations

To estimate the emission rates, mass concentrations and emission flux values must be known. Measured NH_3 concentrations were converted into mass concentrations (C_{mass}). Emission rates were calculated for each individual GLAS using equation (2).

Once the concentration in mass per volume was determined, equations (1) and (2) were used to calculate NH_3 flux and rate, respectively:

$$EFl_{NH_3} = \frac{C_{mass} \times V_{fc}}{A_{FC}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where

C_{mass} = Mass concentration, ($\mu g/m^3$)
EFl_{NH3} = NH_3 gas emission flux ($\mu g/m^2$-s)
V_{fc} = Volumetric flow through the flux chamber (m^3/s)
A_{FC} = Aarea of flux chamber ("footprint", 0.192 m^2)

$$ER = EFlxA_{sc} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where:

ER = Emission rate, kg/day.
EFl_{NH3} = NH_3 gas emission flux ($\mu g/m^2$-s)
A_{sc} = Area of source (GLAS), m^2.

Measured NH_3 concentrations (in ppm) were corrected for NH_3 adsorption through the flux chambers. The procedure for accounting for adsorption losses has been described by Capareda et al. (2005).

Data Analysis Process for Open-lot Dairy

At the open-lot dairy, each corral had areas (dry, shaded and feeding areas) of dispirit cow density and hence varying manure (feces and urine) loading rates. In the summer time, dry area within the corral was marked by minimum cow activity and manure loading while the feeding area had the highest cow activity and manure loading. In the winter time, during NH_3 emission sampling, no one area within the corral was observed to be higher or lower in cow density. The open-lot corral NH_3 data was highly spatially variable for both seasons. A log transformation was used and the data resulted in a normal distribution. After transformation of these data, an F-test on the normalized NH_3 concentrations was performed to assess significant differences among dry, shaded and feeding areas of these corrals. Ammonia concentrations measured from other GLAS at open-lot dairy had normal distributions and therefore, no transformation of these was performed.

Results and Discussion

In 2005, 115 and 109 NH3 concentration samples were collected from the open-lot dairy GLAS in summer and winter seasons, respectively. This dairy had 12 earthen corrals for milking cows. Each corral had similar total area (8570 m^2). In both studies, one corral was randomly chosen to represent all open lots at the dairy. Approximately 170 milking cows were fed in the sampled corral. Preliminary assessment of summer and winter data indicated that overall NH3 emission rates were 41.9 ±3.2 kg.day-1 for the summer and 18.6 ±3.1 kg.day-1 for the winter season. The estimated NH3 emission rate for winter was nearly one half (45%) of that from summer. Lagoons (62%) in summer and open-lot corrals (89%) in winter were the highest contributors to NH3 emission for the open-lot dairy. The difference between the overall emission rates from each season was due to ambient and source temperature variations. Spatial variation of NH3 emission from the open lot earthen corrals was due to different animal density resulting in varying manure loading on the corral area.

Conclusions

The quantification of NH_3 emissions from ground level area sources in a dairy is needed to understand which sources contribute most to the overall NH_3 emissions during winter and summer conditions. Summer and winter NH_3 emissions were estimated from an open-lot dairy.

Ammonia emission rate variations among GLAS occurred due to seasonal changes in ambient and source temperatures, and spatial variations of NH_3 occurred in the open-lot corrals due to varying cow density and the resulting dispirit manure (feces and urine) loading in feeding, dry and shaded area of the open lot. Within the open lot corral, summer NH_3 emissions from the dry area were significantly lower than those from shaded and feeding areas. While winter NH_3 emissions from feeding area were higher than shaded and dry areas, no statistically significant differences were detected in NH_3 emissions from the three divisions of the open-lot corral. Overall, summer NH_3 emissions were nearly twice those of winter emissions. It is necessary to consider both management practices and climate conditions to determine NH_3 emissions from the animal feeding operations.

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The Agricultural Risks in Zone of Heavy Metal Pollution Point Source

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Abstract

The continuous Earth's human population growth imposes the necessity of intensification of agricultural food production aiming to satisfy the increasing demands. Considering that the extension of arable soils has natural limitations, for the agricultural purposes frequently are used the neighbor areas of highly industrialized zones. These zones are potential sources of pollution with different toxicants, especially heavy metals, of the agricultural production grown in such proximity's.

Most of the former Soviet Union countries are mainly agricultural countries. The ecological problems in these countries lack the required attention, thus the negative impacts of industrial activities on the quality of agricultural products remains still poor studied. These phenomena become more acute in the areas of gigantic industrial complexes emplacement, due to its inheritance from the former Soviet Union, home of 1/6 part of the Terra surface.

In the Republic of Moldova, a country located in the South-Eastern part of Europe, aspiring to become a part of EU, the direct or eventual impact of industrial giant activities require thorough research, taking into account the high share of agricultural products in the export.

The acuity of the problem is due to the emplacement in the central zone of the country, densely populated (126 people/km^2) and intensively used for agricultural food production, of a gigantic industrial complex, which includes two cement plants with total annual capacity of 4.4 million t/year, and one metallurgical plant of 1 million tons/year. This industrial complex is located in the proximity's of the Rezina and Rabnitsa cities, on the both banks of the Dniester River. Dniester River, the main water artery of the country, being a transboundary water way, total length of 1352 km, is of great importance for a wide variety of uses as agriculture, industry and source of potable water for about 10 mln. population of Moldova and Ukraine. About 54% general needs for water of the national economy are covered from this river.

This study has been focussed on the evaluation of pollution risks of the agricultural products grown in the neighborhood of heavy metal point pollution source.

The environmental impact of Rezina-Rybnitsa industrial complex (RRIC) is diverse, thus contributing to the aerial, terrestrial and aquatic ecosystems contamination with metals of high toxicity (Hg, Cu, Pb, Cd, Tl) and, consequently, more or less, influencing their content in the agricultural products.

The content study of these toxic elements in water of the Dniester River, Dubasari reservoir (Figure 1) denote that in the proximity of the RRIC (zone with a radius of 10 km) the concentration of investigated heavy metals exceed 2-4 times the downstream level (50 km South). This fact attests that the use of water for irrigation purposes creates risks of heavy metal pollution for agricultural products, especially with mercury and tallium, metals of extreme eco-toxicological hazard.

Heavy-metal pollution of the environment occur by the gaseous-powdered emissions of iron and steel industry activities and cement production facilities what are sedimentated and precipitated on the top soil stratum. Determination of investigated metal concentration in adjacent soils of RRIC (Figure 2) shows the evidential effect of soil pollution in the 10 km radius area. In the epicenter of this zone, the concentration of Hg, Cu, Pb, Cd, Tl exceed approximately 2-11 times the registered level at the 50 km distance south from the point pollution source, preponderantly for the Cd and Hg. Therefore, the agricultural products in this zone are supposed on the risks of toxic metal contamination through the assimilation of the mineral substances from the polluted arable soils.

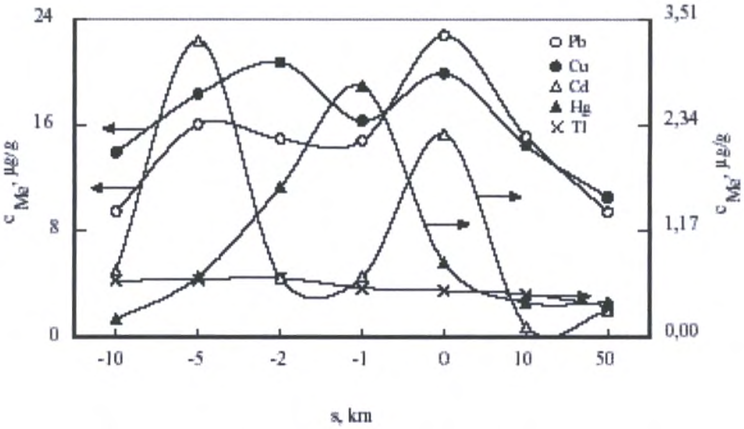

Figure 2. Heavy metals content in adjacent soils of point pollution source zone

It is known that the process of the vegetation of plants is influenced by the ecological state of aerial ecosystem (photosynthesis and carbon authotrophic assimilation). The content level of metals under study has been determined in air, by means of bioindicator species lichens *Xanthoria parietina*, as the content of toxic element in their biomass depends directly to their habitat's contamination level. The results presented in Figure 3 attests the negative impact of RRIC on the aerial ecological state. The natural lichen's biomass in the epicenter area (radius of 10 km) accumulate 2-18 times more then the background samples (50 km South). Hg air pollution (18 times) is dominant.

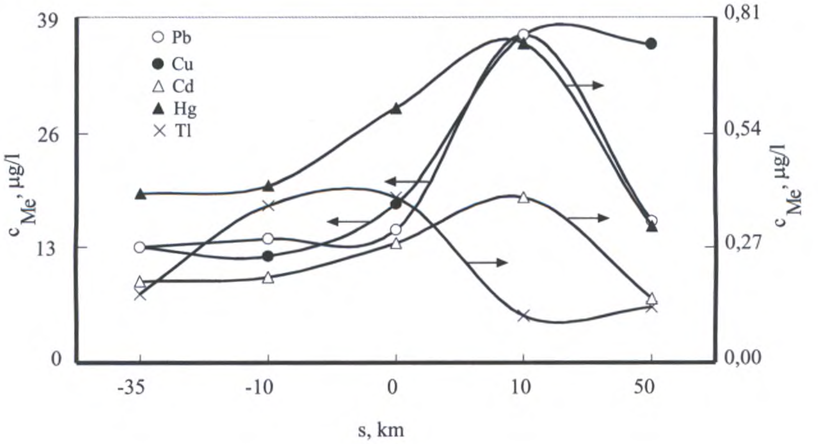

Figure 1. Heavy metals content in water of Dubasari reservoir (Dniester River) in zone of point pollution source. Minus – northeast Rezina city, plus – Southeast.

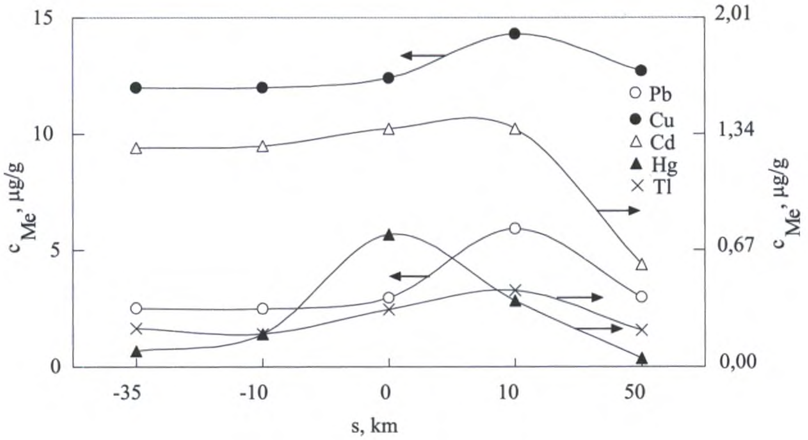

Figure 4. Heavy metals content in *Potamogeton perfoliatus L.* in zone of point pollution source.

Determination of heavy metals content in freshwater vascular plants biomass (*Potamogeton perfoliatus L.*, *Butomus umbellatus L.*), which can serve as a model of intensively irrigated agricultural plants, demonstrate (Figure 4, 5) that these plants intrinsic absorb toxic elements from the environment, consequently the investigated metal content in plants biomass registered maximum values in the same zone that includes RRIC. Mercury is leading of the assimilated pollutant by freshwater vascular plant in this area, accordingly above presented data.

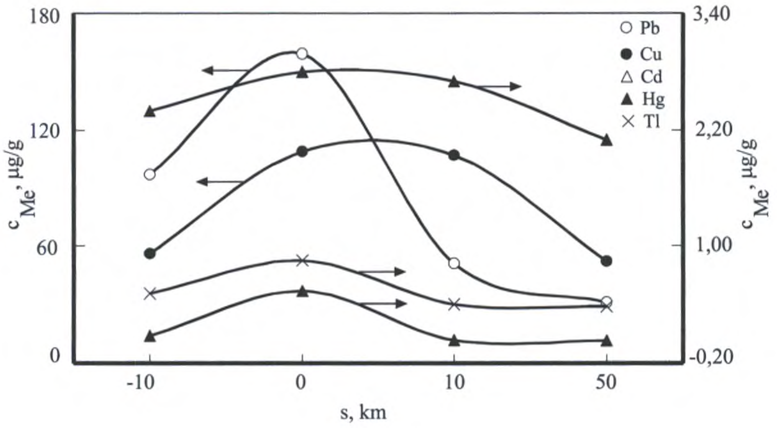

Figure 3. Heavy metals content in lichens *Xanthoria parietina* biomass in zone of point pollution source

For the evaluation of major pathways of metal uptake by plants, the statistical processing of data related to concentration of Hg, Cu, Pb, Cd and content of mineral substances in biomass of the freshwater vascular plants has been done. The results presented in Figure 6 make obvious the strong dependence between the metal content to calcium (Ca) concentration in plants biomass.

We have shown that considering the physiological properties of plants, some heavy metal can be assimilated directly from the atmosphere, facts confirmed by highly positive correlated linear dependence between the Tl and Hg contents in leaves of *Potamogeton perfoliatus L.*, *Butomus umbellatus L.* and in lichens *Xanthoria parietina* biomass (Figure 7)

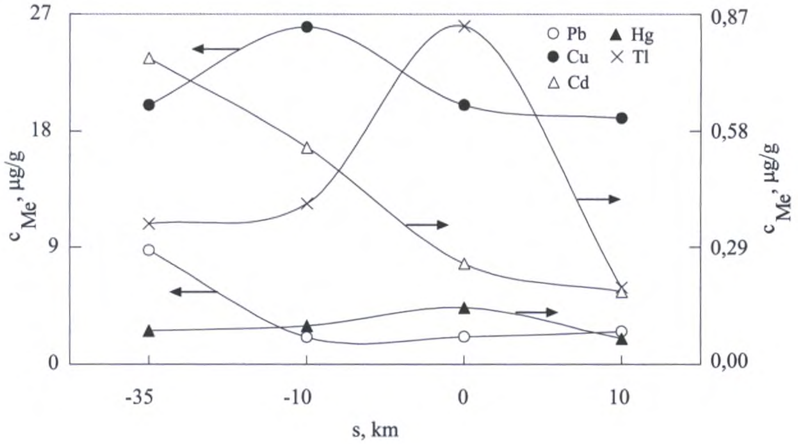

Figure 5. Heavy metals content in *Butomus umbellatus L.* in zone of point pollution source.

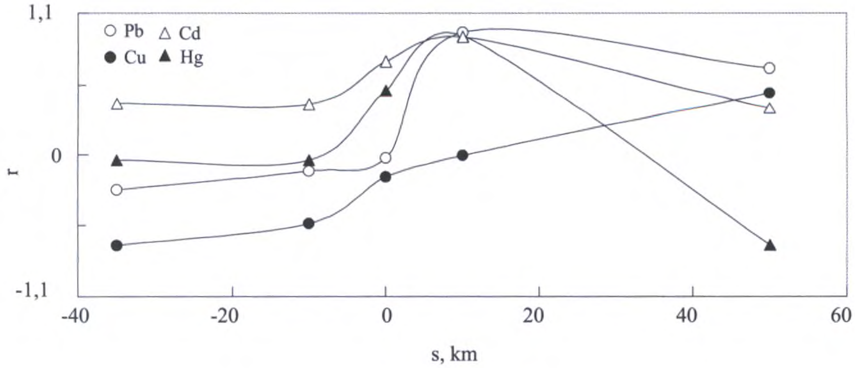

Figure 6. Interdependence between heavy metal and calcium content in freshwater vascular plants biomass in zone of point pollution source

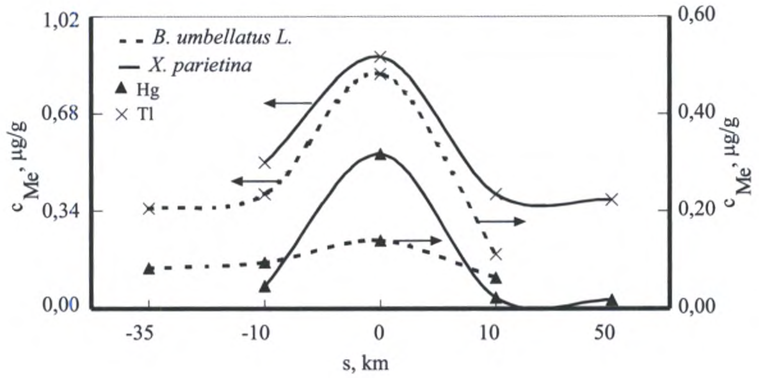

Figure 7. Interdependence between Hg and Tl content in freshwater vascular plant *Butomus umbellatus* L. and lichen *Xanthoria parietina* biomass in zone of point pollution source

The results of performed study allows us to conclude that the agricultural products grown around the Rezina-Rybnitsa industrial complex, an area with a radius of 10 km, are exposed to high risks of heavy metal contamination through polluted air, soil and water. These facts should be considered for the planning activities both of industrial complexes and agricultural lands.

Biofilters Used to Reduce Emissions from Livestock Housing – A Literature Review

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Abstract

This paper reviews the literature on the development of biofilters for use on confined livestock facilities. More specifically the paper addresses the history, current and accepted design parameters, and status of research. Biofilters offer one potential solution to reduce nuisance odors and pollutants emitted from confined livestock housing. Typical biofilters used in agriculture consist of an organic media mixture of wood chips and compost. Barn exhaust air is blown through this media, allowing the microorganisms contained within the media to break down the gaseous compounds. Biofilters have been used in agriculture in Europe since the 1970's and in the United States since the 1990's. Much advancement has been made in terms of biofilter design since their introduction to agriculture. Design parameters have been established to minimize cost and maximize effectiveness. Some of these design parameters include bed thickness, media type, empty bed contact time, moisture control, and media bed orientation. These design parameters also influence factors such as pressure drop, microbial ecology, air channeling, foot print size, and gas/odor removal efficiency. Overall, properly designed biofilters used in agriculture have been shown to reduce hydrogen sulfide emissions by up to 95% and ammonia emissions by up to 65%. Biofilters are an effective air pollution control option for agriculture.

Introduction

Solutions are needed to deal with the problem of odorous compounds and airborne contaminant emitted from animal agriculture. Odor and airborne contaminant emissions have always been a part of the livestock and poultry industry (NRC, 2003). In the past, however, sparse human population and livestock spread out over a large land area made odor less of an issue. Now, with the advent of farms containing large numbers of animals confined to a smaller area; the odorous compounds and contaminants are becoming concentrated. Additionally, many areas zoned agriculture are being inhabited by more non-farm rural residents. This trend results in odor issues for livestock producers that in the past were minor or nonexistent. The urgency of the situation is clearly evident in the number of state, national, and global environmental air pollution regulations being developed.

Solutions are needed to reduce the nuisance value of these odors. One of the more recent practices to reduce odor emissions is the use of biofilters. Biofiltration is not a new technology, but is an adaptation of natural atmosphere-cleaning processes. Biofilters use microorganisms to convert gaseous contaminants to carbon dioxide, water vapor, and organic biomass. They are effective in reducing odorous components found in low concentrations in large quantities of air; thus making biofilters effective to reduce emissions from livestock facilities (Nicolai and Janni, 2000). Biofilters use a porous solid medium to support microorganisms and allow access to the contaminants in the airflow. Air passes through the biofilter media, which is surrounded by a biofilm. The contaminants are sorbed from a gas to an aqueous biofilm where the microbes live. This biofilm is where the microorganisms break down the contaminants. Media consists of relatively inert substances which ensure large surface attachment areas and additional nutrient supply. Examples of media include peat, soil, compost, wood chips, straw, or a combination of two or more (Nicolai and Janni, 2001).

History of Biofilters in Agriculture

Microbial reactions in soils have been occurring naturally for many centuries, but only since the 1950's have such techniques been used to treat waste gases. Extensive biofilter research has been conducted only in the past 35 years, thereby limiting the quanity of information.

Biofilters were used in wastewater treatment plants, chemical manufacturing facilities, composting, and other industrial air pollution schemes before being adapted to agriculture. They were first applied to livestock facilities in Germany in the late 1960's to reduce odor emissions from livestock facilities (Zeisig and Munchen, 1987). In the 1980's biofilters were used to reduce odor from livestock operation in the Netherlands and Sweden (Scholtens et al., 1987; Noren, 1985). These biofilters were based on the Zeisig design and decreased hydrogen sulfide and ammonia by 50%. When moisture content was at an optimum level, the reduction increased to 80%. Scholtens et al., (1987) reported an average filter efficiency of about 70% ammonia removal from biofilters on piggeries and calf sheds in Sweden. Scholtens and Demmers (1991) reported that even though biofilters are effective in treating exhaust air from livestock buildings, they were rarely used in intensive livestock farming in Europe. Their absence was based on 1) the construction and operating costs of treating large quantities of air, 2) the cost of handling effluent water needed to remove nitrogen absorbed in the biofilter material, and 3) the daily performance fluctuation.

Investigation of biofilters for livestock facilities in North America began in the mid 1990's. Nicolai and Janni (1997) investigated the feasibility of treating pit gases from a swine gestation barn. Young et al. (1997) investigated with three pilot-scale biofilters using swine odor and found average reductions of odor intensity, irritation intensity, and unpleasantness were 61%, 58%, and 84% respectively. Odor reductions between 78-80% were measured on two biofilters treating pit gasses from a swine finishing barn (Hartung, 1997). Ammonia reduction was mainly influenced by airflow and moisture content.

Biofilter Types

Biofilters are categorized by the configuration (open or closed) and flow sequence (up-flow, down-flow, or horizontal flow). Devinny et al., (1999) discussed the differences between an open and an enclosed biofilter. A closed system controls both the biofilter outlet and inlet gas streams whereas an open system discharges treated gas from the biofilter directly to the atmosphere. Industrial applications may place biofilters in closed vessels with deep layers of media to save space. These systems may be either up or down flow, depending upon the moisture application system.

Open biofilters are more commonly used for animal agricultural. They are less expensive than closed systems, have relatively thin layers of media to reduce backpressure on the air handler, are outdoors, and are usually quite large in terms of surface area exposed to the atmosphere. Horizontal media beds (up or down flow) and vertical media beds (horizontal flow) are used, depending upon surface area and space availability (Lefers and Nicolai, 2005).

Up-flow open biofilters are the most common biofilter used in livestock production since they are generally more economical. Most livestock building ventilation fans exhaust at or near ground level. Therefore to reduce air ducting costs, the air entering the biofilter media should be at this height. Spreading the media out horizontally instead of vertically also saves on construction costs as well. Spreading the media out horizontally may not always be an option, depending on land surface area space available near the production facility. In this case vertical media beds (horizontal flow) may be an option. By leaving the biofilters open to the atmosphere, producers are able to reduce pressure drops, saving on fan electricity bills.

Microbial Activity in Biofilters

Since it is the microorganisms in the biofilter provide the actual work of breaking down the odorous compounds (or oxidation potential), it is important to understand the transformations and interaction of these microorganisms. Our knowledge of microorganisms' ecosystem is fragmentary and poor (Devinny, 1999). Biofilters may be self-inoculating, inoculated with activated sludge or compost, or induced with bacteria species. Most biofilters used in agricultural settings use compost as the source of microorganisms.

Ding et al., (2000) studied the microbial ecology and performance of a biofilter. Their research indicated that introduction of new pollutant gasses into an already operating biofilter did not adversely affect the removal efficiency of the biofilter for the pollutant gasses already being treated. The research also showed that changes in the microbial community occurred with changes in the inlet gasses. Thus, the research demonstrated the ability of the microbial community to respond to changes in the inlet gasses without affecting treatment of those gasses.

Sakano and Kerkhof (1998) studied the changes in a microbial community structure of a biofilter used to treat only ammonia. They found that the overall diversity of the heterotrophic microbial population had decreased by the end of the experiment. The community structure of the heterotrophic population had also shifted between subdivisions. This experiment also showed the ability of microbial communities in biofilters to adapt to changes (or lack thereof) in inlet gasses.

Joshi et al. (2000) studied the gaseous ammonia removal of laboratory-scale biofilters. Their work showed that 95% of ammonia was degraded to NO_3 and NO_2 in the quarter of the biofilter closest to the inlet gas stream after eight days of operation.

Sadowsky et al. (1999) investigated the culturable bacteria in biofilter material that was treating exhaust air from a swine barn. They found the media material did not contain significant numbers of enteric coliforms or salmonella and concluded that sterilization and special disposal of biofilter material is not necessary. This is similar to results found by Pillai et al. (1996), who reported that while air samples at sludge application sites contain relatively high numbers of heterotrophic bacteria (averaging 10^5 CFU/m^3), no sites contained airborne fecal coliforms or salmonella.

Further work is needed to understand the relationship between microbial community dynamics and biofilter performance. Research needs to be done to determine how fast microbial communities change in response to changes in inlet gas concentrations. However, this research should not affect biofilter design dramatically, since a sufficient amount of media to host the number of microorganisms needed to effectively remove odorous compounds is established by the EBCT (Devinny et al., 1999).

Biofilter Residence Time

In order to get maximum odor reduction from a biofilter, the air passing through the filter must contact the filter media for a given amount of time. This amount of time is known as the residence time or empty bed contact time (EBCT). It is defined as the empty bed filter volume divided by the air flow rate (Devinny et al., 1999).

The correct residence time is an important variable to know in the design of an efficient biofilter. Zeisig and Munchen (1987) showed sufficient odor reduction at 5 seconds for pigs and 3 seconds for chickens. Pearson (1990) used 20 seconds while doing his cost estimates for biofilters on swine and poultry operations. Nicolai and Janni (1998) did a study to see if there was any statistical difference between a 4 second and 8 second residence time for a swine nursery barn, and concluded that 4 seconds was adequate. In a further study by Nicolai and Janni (1999), it was determined that there was no significant increase in odor reduction with residence times of 6 seconds or more for either dairy or swine. However, odor reduction was less than optimal at less than 4 second residence times. A recommended design residence time for a biofilter on a dairy and swine facility was given at 5 seconds for adequate odor and hydrogen sulfide reduction (Nicolai et al., 2004).

Pressure Drop

Agricultural ventilation fans generally are designed to operate at less than 62 pa (0.25 in H_2O) (Nicolai and Janni, 1998). If the pressure drop through the biofilter can be kept less than 40 pa (0.16 in H_20) it may not be necessary to replace existing fans in a livestock building when installing a biofilter (Phillips et al., 1995). Thus, pressure drop becomes a very important factor in the design of a biofilter.

In a study of various types of packing media for biofilters (heather, mixture of heather and coconut fiber, mixture of heather and fibrous peat, bean straw, coconut fiber, linseed straw, and screened wood chips), Phillips et al. (1995) concluded that wood chips over 75mm screen size appeared to be the most promising because they gave one of the lowest pressure drops and were the least compressible.

The compost/kidney bean straw mixture used by Nicolai and Janni (1997) had a maximum pressure drop of 47 pa reported after six months of settling. In a 2001 study conducted by Nicolai and Janni on different mixtures of wood chips and compost, findings indicated that pressure drop increased as the percent of compost in the mixture increased. Further research by Nicolai and Janni (2001) indicated that the pressure drop is related to the percent voids space in the biofilter media and the airflow/surface area relationship in the biofilter itself. A recommended mixture of 20 to 30% compost and 70 to 80% woodchips by weight was given as optimal for an agricultural biofilter (Schmidt et al., 2004). The results from this study allow sizing of a biofilter and provide guidance in selecting fans with adequate performance characteristics for the expected pressure drop. Nicolai and Janni (2002) developed a graph that shows the relationship between media void ratio, airflow, and pressure drop.

Biofilter Moisture

Biofilter moisture has been cited as one of the two key factors influencing biofilter performance, along with contact (residence) time (Schmidt et al., 2004). In fact, lack of control over media moisture has been cited as the cause of up to 75% of all biofiltration problems (Reyes et. al., 2000, and Boyette, 1999). Dry media causes channeling and leads to a decrease in biological activity. Media drying is especially a problem in the summer, when an increase in temperature raises the water capacity of the air, causing a faster evaporation rate of water from the media (Schmidt et al., 2004). Biofilters with higher moisture contents and longer retention times were shown to have the best removal of both ammonia and hydrogen sulfide (Sun et al., 2000).

Nicolai and Janni's (2001) study on biofilter media mixture ratio found that media moisture content influenced odor, hydrogen sulfide, and ammonia removal efficiency. This study recommended a moisture range from 35% to 65% for efficient pollutant reduction using compost and wood chips. Optimum biofilter moisture content for a compost/wood chip mixture has been given as 50% (Schmidt et al., 2004). Similarly Boyette (1999) recommends 50 to 55 percent moisture is a good target range for a compost-based biofilter media.

Moisture addition can be needed during mild and warm weather (Nicolai and Janni, 1997). A Korean study on a biofilter using pine chaff and perlite as filter media found that removal rate of odor drastically reduced when the moisture content dropped below 60% (Chang et al., 2004). Lack of a sensor to keep stable moisture contents was cited as the reason efficient odor removal was not achieved.

A number of moisture sensors and systems have been tried to measure biofilter moisture. Classen et al. (2000) used a weight-based method of calculating moisture content on three pilot-scale biofilter units by continuously weighing each biofilter. This method was found to maintain the proper moisture level on each of the three biofilter units within 4%. However, the weight-based method could only be used because dust was excluded from the biofilter. Most agricultural applications have dust loading from the air being treated by the biofilter, which contributes to the problem for a weight-based method. Also decomposition of media resulting in losses in bed weight could be assumed to be caused only by losses of moisture. However, periodic re-calibration could compensate for media degradation and washout (Reyes et al., 2000). An additional problem with a weight based system is caused by the uneven distribution of moisture in the filter. The weight system reports the average moisture content in the bed but some sections may be too dry resulting in air channeling.

Reyes et al. (2000) demonstrated that a TDR probe could be used to monitor biofilter media moisture content on a real time basis. However, this experiment was done using 60% compost and 40% pearlite, a mixture that is not used for most agricultural biofilters because of excessive pressure drops.

Researchers at the University of Illinois (Funk et al., 2005) found soil and hay moisture meters inadequate for sensing agricultural biofilter moisture content because of poor media to probe contact. They also found that relative humidity sensors were of some value. An electrical capacitor type moisture sensor for determining moisture content in biofilters is being developed, with preliminary tests indicating it could be useful for monitoring biofilter moisture (Funk et al., 2005).

Lefers and Nicolai (2005) have used a watermark moisture sensor and control system to control moisture in a laboratory-scale biofilter with promising results. This research showed that a watermark sensor may be used effectively to control moisture in a lab scale biofilter. Further testing in a full scale agricultural biofilter is needed.

Moisture content has also been shown to have an effect on the pressure drop through biofilters (Nicolai and Janni, 2001). Pressure drops are higher when moisture content is higher. However, this effect is only noticeable on low compost to wood chip ratios, and is not a major factor on pressure drop through media that consists of high compost to wood chip ratios.

Biofilter Media Depth

The biofilter media depth will also have an effect on pressure drop. Less media depth results in reduced pressure drop which is linearly correlated with media depth (Sadaka et al., 2002). Media depth also effects odor reduction efficiency. Nicolai and Janni's (1999) study on biofilter retention time showed decreasing media depth below 0.15 m reduced odor and hydrogen reduction below 65%. As a result they recommended minimum depth of a compost/wood chip media biofilter between 0.15 m and 0.3 m, with an estimated ideal minimum depth at 0.25 m. Findings based on research done on the spatial structure of microbial communities in peat biofilter media have indicated that 75% of inlet concentrations of aromatic compounds were degraded between 0.3 and 1 m in depth (Khammar et al., 2005). For biofilter design in agriculture, media depth is recommended to remain between 0.25 m and 0.45 m to reduce the possibility of large pressure drops, compaction, excessive drying and air channeling (Schmidt et al., 2004).

Effect of Temperature on Biofilters

The microorganisms in the biofilters are living beings, and as such must be maintained at a certain temperature to sustain life. The microorganisms that are most effective in the degradation of odor compounds are mesothermic and have an optimum operating temperature between 30 and 40 degrees C (Janni and Nicolai, 2000). In a study on an agricultural biofilter exposed to atmospheric conditions in Alberta, Canada, it was found that differences in treatment temperature had no apparent influence on odor removal (Clark et al., 2004). Treatment temperature generally ranged between 15 and 30 degree C because the biofilter was insulated to prevent heat loss during the winter. However, data in the experiment did suggest that higher operating temperatures accelerated the establishment of microbial populations and the start of effective biofiltration. In a study conducted in Manitoba, Canada, an open biofilter was evaluated for treatment of odor during sub-zero ambient temperatures (Mann et al, 2002.). This study found that at ambient temperatures below -20 degrees C, biofilter bed temperatures were maintained at around 16 degrees C without the need for insulation or supplemental heat. Heat was provided by the warm exhaust air from the swine barn, and was adequate enough to ensure microbial survival during even the coldest winter days. There was also no apparent reduction in biofilter effectiveness during the winter months.

Biofilters on manure storages or unheated buildings may freeze in winter, which temporarily reduces the effectiveness of the biofilter (Schmidt et al., 2004). However, as the biofilter again thaws in the spring, the microorganisms again become active and the removal efficiency is restored.

Degradation of Biofilter Media

The same microorganisms in the biofilter that treat the odorous compounds in the exhaust air also degrade biofilter media as a result of their activity (Wani et al., 1998). Because of this, the biofilter settles and becomes compacted over time, reducing component interchange surface and increasing the resistance to flow. Media dry matter may even increase over time as a result of growth of microorganisms and chemical accumulation in the media due to mineralization (Sun et al., 2000). Eventually, the biofilter suffers too much from aging effects and the media must be replaced. No long term studies have been completed on compost/wood chip biofilters treating air from livestock buildings to determine the length of media life, but it is estimated that most biofilter media will remain effective without causing a large pressure drop for 3 to 10 years or more (Schmidt et al., 2004).

Horizontal Airflow Biofilters

Most agricultural biofilters are vertical airflow biofilters which may result in a large footprint. Because of space limitations for some installations, vertical flow (also called horizontal bed) biofilters may not a viable option for agricultural applications.

An alternative to vertical flow biofilter is to use a horizontal airflow (vertical bed) biofilter. These filters have a smaller footprint since the bed is spaced vertically instead of horizontally (Garlinski and Mann, 2003). Resistance to airflow in the horizontal direction was shown to be approximately 0.65 times the resistance to airflow in the vertical direction (Sadaka et al., 2002). This means a lower pressure drop for vertical bed biofilters, which could in turn result in lower energy consumption.

However, the disadvantage associated with vertical bed biofilters is the compost will settle and become denser over time causing a increase in pressure drop (Devinny et al., 1999). A larger pressure drop through the media is caused by the natural settling of the filter bed (Zeisig and Munchen, 1987). Compaction of a biofilter can cause serious problems because the odorous gases flow through the space yielded by the compaction (Choi et al., 2003). This channeling can lead to an increase in local drying, which allows untreated air to exit from the biofilter, reducing overall efficiency. Significant media settling has occurred with horizontal-airflow biofilters when wood chip-based media is used (Garlinski and Mann, 2004). The settling results in more air leaving through the low pressure drop areas at the top of the filter. Non-uniform airflow through the biofilter media will cause the residence time to be affected, reducing the odor removal efficiency of the vertical bed biofilter.

A solution to the settling that occurs in vertical bed biofilters is to taper the media bed of the biofilter so that the media wall is thicker at the top than the bottom. This leads to a decrease in channeling and a more uniform airflow through the biofilter over a period of time, which results in improved efficiency. Lefers (2006) showed that a taper angle of 9.6 degrees provided the most uniform airflow through the biofilter bed after media settling.

Biofilter Costs

Pearson (1990) reported on studies conducted in Europe that showed biofilters were effective in their performance, but needed to be more cost effective before being adopted by the livestock industry. The report demonstrated that biofilters were the most effective and the least cost device for odor control compared to bioscrubber, mopscrubber, packed tower, or sprayscrubber. In spite of this, the report reasoned that even the biofilter was still out of the price range of most producers. The report estimated that the biofilter would add 6% to the production cost of pigs and 20% to the production cost of poultry using heather as the biofilter media. However, the report also speculated that differences in construction could reduce the costs involved.

O'Neill et al. (1992a) evaluated twelve odor abatement systems for costs to treat odor emissions from mechanically ventilated livestock buildings. The seven systems judged to be effective include chemical or biological treatments of air leaving the building. Chemical treatments were found to be prohibitively expensive. Biological treatments were much lower cost and the lowest cost treatment system was found to be a biofilter.

In the United States, the cost for biofilters used in an agricultural application was investigated. Nicolai and Janni (1997) reported on a biofilter that was effectively developed for full scale mechanically ventilated production swine units with deep manure pits below a slatted floor. This research estimated the construction and operating cost of a swine biofilter at $0.28 per piglet produced. The biofilter media used for this study was 50% red kidney bean straw and 50% compost by weight. This biofilter had an odor threshold reduction by an average of 78%, hydrogen sulfide reduction by an average of 86% and ammonia reductions of an average of 50%.

Nicolai and Janni's (1998) research indicated a total installation cost of about $0.22 per piglet or $0.062 per cfm when installed on a swine gestation barn. Operating costs were also estimated at $275 per year for effective rodent control program and $125 a year for water sprinkling of biofilter media and using higher power ventilation fans. The biofilter media for this study consisted of a mixture of 50% yard waste compost and 50% brush wood chips by weight and effectively removed 82% of the odor and 80% of the hydrogen sulfide. The report concluded that while these costs could be affordable by most swine producers, it was more than the value producers were currently spending to control odor.

Higher biofilter cost on European pig units may be attributed to the location of the building exhausts ventilation fans. Many livestock buildings utilize a chimney system through the roof to exhaust the air, adding cost to duct the air back down to a biofilter located on the ground. In the U.S. most facilities exhaust air near ground level through wall or pit fans. A shorter and simpler duct to move the air to a biofilter results in a lower cost.

Conclusions

A review of the literature reveals considerable advancements have been made in biofilters for agricultural applications in the last 35 years. When designed correctly, biofilters have demonstrated to be an effective odor (up to 95%) and air pollution control option for livestock producers.

There remains research to be conducted that would further improve biofilter efficiency in agricultural applications. As an example, research is needed in testing and developing a moisture sensor and moisture control system for use on full scale agricultural biofilters. Also, research is needed to determine the length of time needed before the media requires replacement.

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Isotopic and Back Trajectory Analysis on Rainfall Chemistry for Developing Source-Receptor Relationships in Fine Particulate Matter Formation

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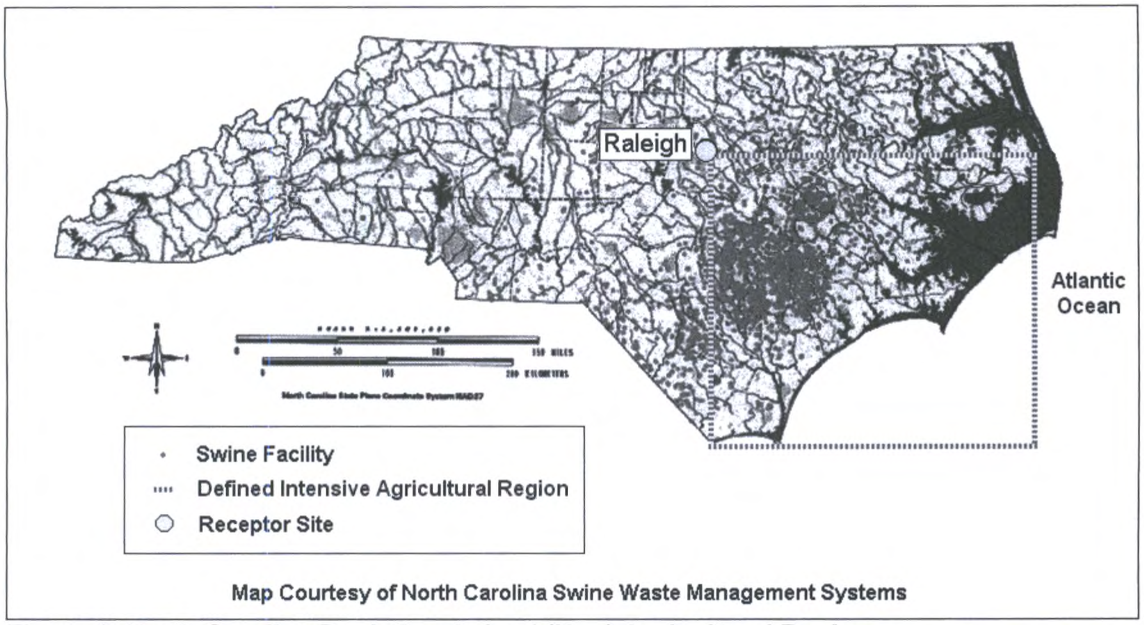
Abstract

Nitrogen oxides (NO_x = NO + NO_2), nitrate (NO_3^-), ammonia (NH_3), and ammonium (NH_4^+) have important effects on rainfall acidity and fine particulate matter ($PM_{2.5}$) formation. The agricultural corridor (figure 1) of southeast North Carolina, which includes approximately 10 million hogs, acts as a major source for these pollutants. Previous studies indicate, for example, that up to a 50% increase in ammonium concentrations in Raleigh rainfall occurs during periods when air masses cross the animal agricultural area. The biological activity associated with farming in the region also produces pollutants with heavily depleted nitrogen isotope ratios (low delta ^{15}N values), suggesting that it may be possible to verify that a biological source of pollutants is in fact being detected at a receptor.



Map Courtesy of North Carolina Swine Waste Management Systems

Figure 1: North Carolina Depicting Animal (Hog) Agricultural Region

The Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to determine potential sources of nitrogen in rainwater collected at an urban site in Raleigh, North Carolina, during the first three quarters of 2004. The delta ^{15}N isotope ratio signatures of each sample were used to further differentiate between sources of the same compound. This study examined the importance of pollutant sources such as animal agricultural activity (figure 1) and the role of costal meteorology on rainfall chemistry as well as their implications on fine particulate matter formation.

Preliminary Results

Samples that transited across the dense crop and animal (swine) agricultural region had no significant statistical difference in nitrate concentrations overall (figure 2), but had lower delta ^{15}N isotope ratios (denoted delta N-15 in figure 3) in the nitrate ion averaging -2.1 ± 1.7 per mil than those which averaged 0.1 ± 3.0 per mil from the nonagricultural counterparts. This indicated that it was possible to determine that transport of pollutants from the farm region did occur, without usable information about concentration. However, the limited data set does not offer any conclusive evidence of similar patterns in ammonium ions. An increase in PM fine mass concentrations was also found to correspond to air transport over the hog farm regions. For the dates when air was transported to Raleigh from the agricultural area, $PM_{2.5}$ concentrations at the Raleigh (Wake County Department of Air Quality) site averaged 15.1 ± 5.8 $\mu g/m^3$ yearly compared to a yearly average of 11.7 ± 5.8 $\mu g/m^3$ for air which was not (figure 4).

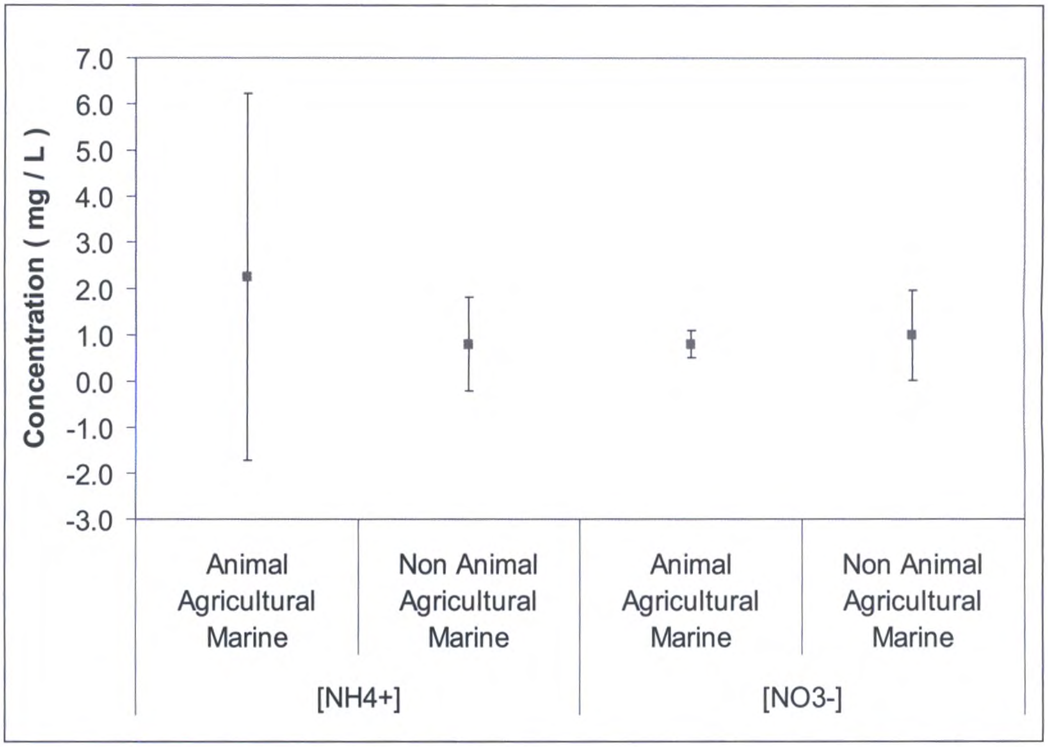


Figure 2: Average Pollutant Concentrations in Rainfall in Raleigh, N.C. for the Easterly Wind Sector

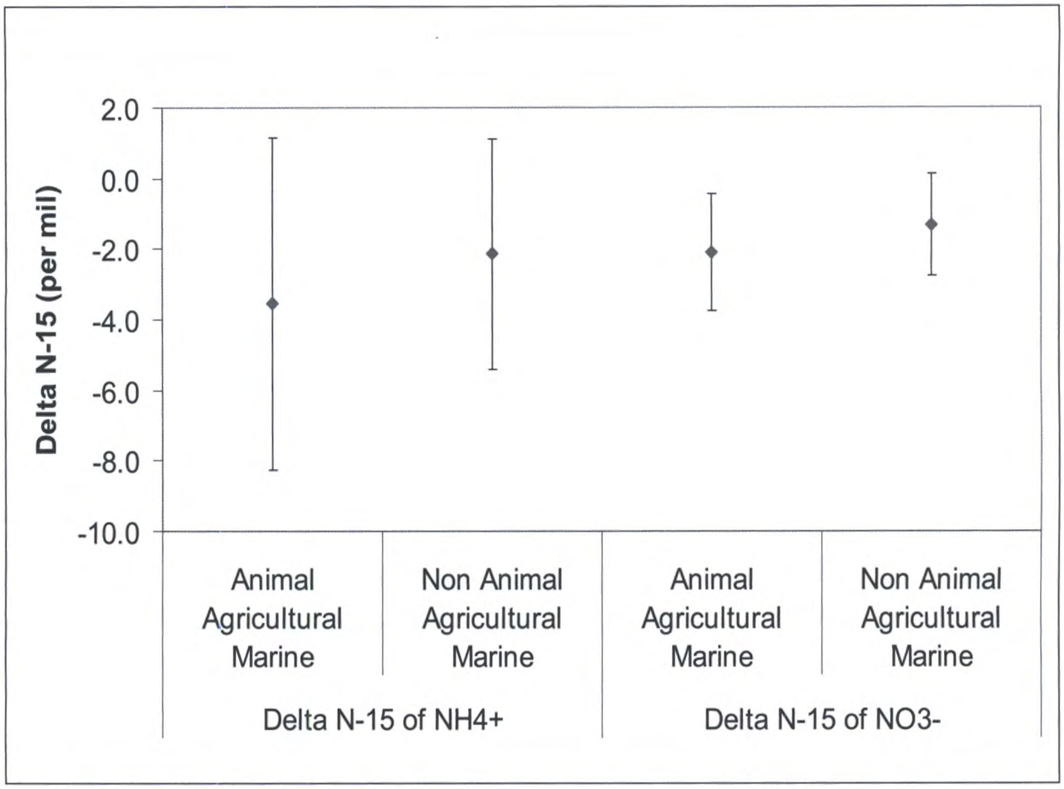


Figure 3: Average Delta ^{15}N Values in Rainfall for the Easterly Wind Sector

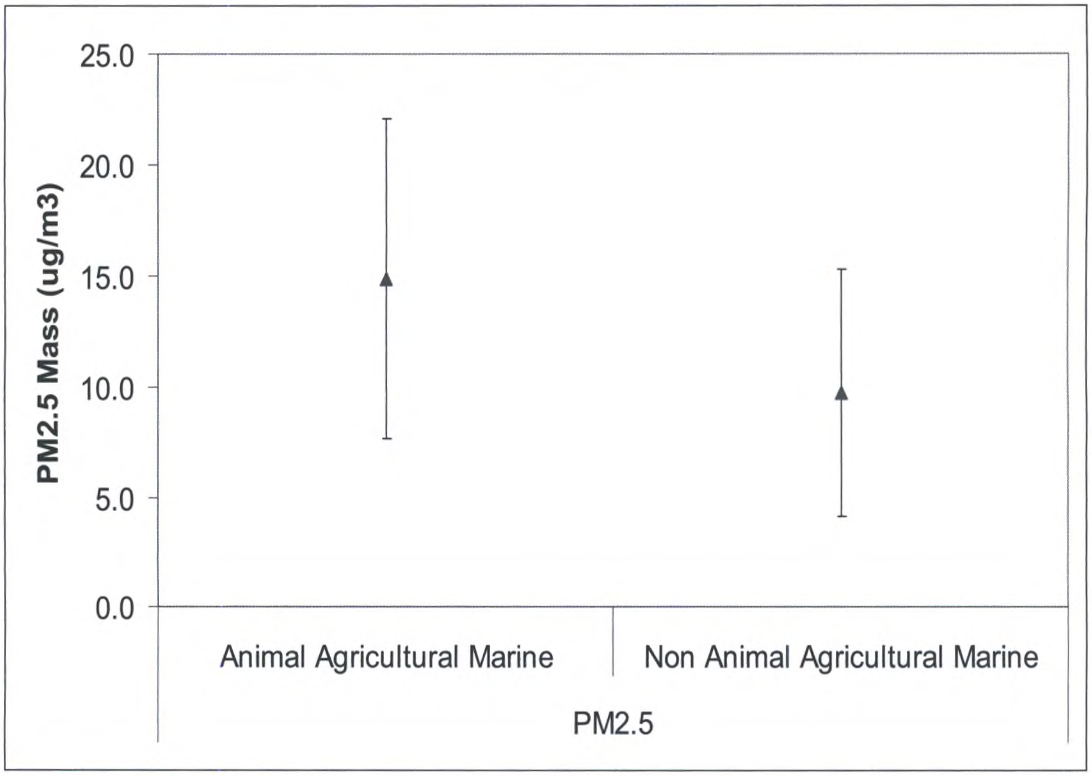


Figure 4: Average Fine Particulate Matter ($PM_{2.5}$) Mass for the Easterly Wind Sector

Future Work

Similar correlations in regional fine particulate matter isotope and chemical composition have also been investigated, though results are not yet available. Studies linking the agricultural corridor's regional air quality with the air found in Wilmington, NC (a frequent receptor of such air according to HYSPLIT forward trajectory results) may provide evidence that increases in pollutants in Wilmington are in fact associated with transit across the farming region. Previous trajectory and pollutant information hinted at the association between such transport and increases in ammonia.

Conclusions

Results indicated that concentration, isotope, and fine particulate matter mass data were to some degree dependent on the trajectory which air at the receptor had traversed. Ammonium concentrations, nitrate isotope ratios, and fine PM mass concentrations support previous claims that there is a strong source – receptor relationship between pollutants emitted from the agricultural corridor and the air received in Raleigh. Low numbers of samples stymied the attempts to study several additional methods of verifying the results; however these may be remedied by continued collection of samples in the region.

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Estimation of Wind Speed Frequency Distribution Application in Predicting Wind Erosion

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Abstract

Wind erosion is a particular serious problem on many lands, and human impact on the global environment and it is an issue of international concern. To adequately predict the consequences of various land management strategies on wind erosion, new technology is needed. Wind transport moisture and heat in the atmosphere and therefore has some effect on the crop production. It also influences rates of evapo-transpiration and directly exacts pressure on crops along its path. Wind may encourage soil erosion when the speed exceeds some critical threshold value for a given soil environment. Crops may be buried by wind blow or dust while the stems and leaves of the tall crops surface abrasion by sand particles. This was part of the surface energy balance project over a bare soil at a humid tropical site at Ile- Ife, Nigeria.

Investigation of Source Regions and Temporal Variation of Ammonia Over the Eastern Mediterranean Atmosphere

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Abstract

Approximately 1500 aerosol samples were analyzed by Unicam 8625 UV-VIS Spectrometer to measure the ammonium ion contents of the samples collected between 1992 and 2000. Samples were collected on Whatman-41, cellulose filters at the Turkish Mediterranean coast by means of Hi-Vol sampler. Major ion content, namely, SO_4^{2-}, NO_3^- and Cl^-, of the samples were also detected by Ion Chromatography (IC). Besides, trace element contents of the collected samples were determined by using Energy Dispersive X-Ray Fluorescence Technique (EDXRF). Long and short term trends of the measures species were investigated. High concentrations of NH_4^+ were detected particularly for summer season. Gaseous ammonia is the predominant atmospheric base and plays an important role in atmospheric chemistry. Ammonia, while not hazardous at atmospheric levels, participates in aerosol formation with HNO_3 and hence can neutralize the acidity of gaseous and particle phase acids. The reason of high background concentration of NH_4^+ during summer might be attributed to the increasing use of fertilizers in this season. In contrast to NH_4^+, high sulfate and nitrate concentrations were measured in the summer season, which could be explained by the increase of solar flux during this period of the year. Trace element contents of the analyzed samples were also showed very clear seasonal variation, for instance, elements originated from crustal sources were high in summer season due to the dryness of the soil; however, marine originated elements were high in winter season, due to the dominance of bubble bursting process over the sea surface. Finally, some statistical techniques such as Positive Matrix Factorization (PMF) and Potential Source Contribution Function (PSCF) were utilized to find the types and locations of sources affecting atmospheric composition of particles in the Eastern Mediterranean atmosphere.

Forecasting the Arrival of Soybean Rust in the Continental United States Using a High Resolution Mesoscale Model and a Dispersion/Deposition Model

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Abstract

On November 10, 2004, the United States Department of Agriculture announced that soybean rust (*Phakopsora Pachyrhizi*) has been detected for the first time in United States. This fungal disease has invaded all major soybean production regions of the world and caused billions dollar in losses each year in South America, Africa, and Asia. The introduction of soybean rust into the United States has the potential of causing $2 billion dollars of yield losses if a major epidemic occurs. Extending a pollen forecasting technique, we have developed a method that accurately forecasted the arrival of soybean rust in the continental United States. This paper describes the methodology used to forecast and diagnose soybean rust transport mechanisms. The results show that this methodology is capable of predicting the locations of soybean rust infestations months in advance based meteorological conditions and disease source distribution. This forecasting methodology indicated that the cloudiness and heavy rainfall associated with tropical storms is the key factor in determining the spore viability and the abnormally large number of hurricanes was likely responsible for the invasion the disease. The technique used to forecast the arrival of soybean rust in the United States can also be used to forecast the spread of soybean rust in the United States.

Introduction

Asian soybean rust (*Phakopsora Pachyrhizi*) was confirmed on soybean plants in Louisiana on November 10, 2004 (see Fig. 1) and has since been discovered in five other states: Alabama, Mississippi, Florida, Georgia and Arkansas (USDA/APHIS). The continental United States is the last major soybean production region affected by the disease. Soybean rust was first detected in the Northern Hemisphere in Cali (at 3.7°N, 76°W), Columbia in August 2004,. The disease was first recorded in Japan in 1903, and identified for the first time in the Western Hemisphere in Hawaii in 1994. In 1996, the disease moved from Asia into Uganda, and by 2001, it had spread throughout much of Africa (Pivonia *et al,* 2004). In 2001, soybean rust was found in South America, and it has spread throughout the soybean growing areas of Brazil, Paraguay, and Bolivia. By 2003, rust had also spread to a northern, non-soybean growing area of Argentina. Severe outbreaks in the last few years in South America have heightened concern for the spread of the disease to the North American soybean. This aggressive fungal disease can reduce soybean yields by as much as 80 percent in individual field if growing conditions are favorable for its spread (Yang *et al.*; 1991). A conservative prediction indicated losses greater than 10% in nearly all the U.S. growing areas with losses up to 50% in the Mississippi delta and southeastern coastal states (Yang *et al.*; 1991).

Knowing when and where the first infection occurs provides the opportunity to control the spread of the pathogen. Although, soybean rust infections can be managed by the proper application of fungicides, the application of the fungicides is time critical and expensive. Spraying fields unnecessarily is expensive and spraying at the wrong time provides no protection to the fields. Correct application requires knowledge of which fields are infected and when.

Since the risk associated with the spread of soybean rust is high a method of forecasting which fields are infected and when would provide growers the necessary information to properly apply fungicides to protect their fields. Two approaches to the prediction of the long-distance dispersal of the soybean rust pathogen can be taken. The first is a statistical, based climatological atmospheric movement. Trajectories of SBR movement using climatological conditions of spore were used by Isard, *et al,* 2003. Although this approach can give a general climatological map of disease movement, it cannot predict the extreme events, which is more typical of disease dispersal (Nagarajan and Singh 1990; Nagarajan et al 1976). The second approach makes use of numerical model to predict the air movement, based theoretical governing equations. This method can predict extreme events since the model equations predict the actual atmosphere rather than a long-term average atmosphere created via the statistical approach described earlier. The obvious disadvantage with modeling approach that the model's predictions are not always accurate. In principle a third approach is to combine the modeling and statistical approaches. This paper describes the second dynamic modeling approach.

We extend the methodology developed by Pasken and Pietrowicz (2005) and Pietrowicz and Pasken (2002) for forecasting pollen concentrations, to forecast the spread of soybean rust on hemispheric scale. We have combined a global-scale long-term forecast model with their pollen forecasting methodology to create a forecast of when soybean rust would arrive in the United States from the southern hemisphere. Initial experiments conducted in 2003 indicated that risk of SBR migrating to the continental United States via atmospheric dispersion from South America was small and if SBR were to be found in the continental United States, it would have to enter by crossing the Central American land bridge. The situation changed dramatically during 2004. Forecasts created during the summer of 2004 showed significant spore concentrations in the southern United States during August and September. These maps projected that SBR would be transported from South America to the southern United States during the intense 2004 hurricane season. This forecast was verified November 10, 2005 when the United States Department of Agriculture announced that soybean plants in Louisiana had been infected with Phakopsora pachyrhizi. Although our forecast cannot be fully tested without ground truth measurements of SBR spore concentrations, these forecasts were verified by comparing forecasts with soybean dispersion computed from meteorological data collected after the forecast, most favorable pathway frequency computations and from USDA data.

Methodology

We have chosen to forecast the dispersion of SBR via a coupled model system. Meteorological models are used to create the data needed by the transport/dispersion/deposition model. Two meteorological models are used. The first is a global-scale long-term coarse-resolution model, which provides the boundary conditions for a second, higher-resolution model. Long-term prediction of the state of the atmosphere is a very challenging problem and most often is done at much coarser spatial and temporal scales than required by the dispersion models. Meso-β or γ scale models provide the necessary high-resolution spatial and temporal forecasts, but only over short periods. Coupling these two modeling systems provides a means to create high spatial and temporal resolution meteorological data over a 60-to-80 day period. We have chosen to couple the global-scale climate model from the Scripps Institution of Oceanography's Experimental Climate Prediction Center (ECPC) model to provide the long-term lateral boundary conditions with the National Center for Atmospheric Research's MM5 mesoscale model. The high spatial and temporal scale meteorological data is then used as input to the National Oceanographic and Atmospheric Administration's (NOAA) HYSPLIT_4, one of the most advanced modeling system for trajectories, dispersion and deposition available.

Meteorological Models

As noted, our coupled modeling system requires a large-scale global model to provide the lateral boundary conditions needed by the regional scale model that produces the high spatial and temporal resolution seasonal meteorological forecast. We adopted large-scale model from the ECPC to provide 6-hourly forecasts up to 16 weeks into future (Roads et al. 2001). We coupled the global scale ECPC model with MM5 to generate the high spatial and temporal distribution forecast of meteorological parameters to produce the meteorological features affect transport, diffusion and deposition of particulates, such as soybean rust. MM5, developed by the Pennsylvania State University and the National Center for Atmospheric Research (NCAR), was chosen because of the flexibility the model provides in forecasting the meteorological fields (Dudhia *et al.*; 2001). The MM5 model has seven Planetary Boundary Layer (PBL) schemes, six cumulus parameterizations, three land surface models as well as many other physics options. MM5 supports the two-way nesting of domains allowing covering large-scale transport phenomena across Americas and at the same time to resolve fine-scale source distribution of soybean fields. The outer most domains were configured with 23 vertical layers with 127x97 grid points centered at 1.0°N, 76.0°W with a horizontal resolution 120 km. The inner nested domain covers the Central America including southeastern U.S. with a resolution of 40km. The lateral boundary conditions were imposed by considering an 11-grid-point nudging zone adjacent to each lateral boundary where the weighting of the observed data was reduced linearly away from the boundaries to the interior of the model domain.

MM5 allows the number of layers in the model to best suit the forecasters' needs and it includes a land surface model that includes vegetation, soil types and deep soil temperatures. We chose the 24-category database and physical parameters for the western hemisphere. MM5 has been extensively tested by the meteorological community and has a reputation for producing high quality forecasts. The MM5/PSU modeling system has been successfully used for a broad spectrum of studies ranging from theoretical to real-time studies. These results have been carefully studied to test the accuracy of the modeling system. These studies show that the MM5/PSU modeling system is the best performing modeling system for meso-α and meso-γ scale studies.

HYSPLIT_4 Model

The National Oceanic and Atmospheric Administration, NOAA, and Air Resources Laboratory's HYSPLIT_4 (Draxler and Hess, 1998), which has been under development since 1982, was used to calculate the transport/diffusion and deposition of the SBR spores. HYSPLIT_4 uses gridded model output or a series of gridded meteorological fields from a variety of sources , such as Eta Data Analysis System (EDAS) or output of a forecast model such as MM5/PSU, Eta, AVN or other NCEP models as input. The model uses a hybrid between the Eulerian and Lagrangian coordinates to calculate trajectories and dispersion of air parcels. Particle advection and diffusion calculations are made in a Lagrangian framework while concentrations are calculated on a fixed grid. Air concentration calculations associate the mass of the airborne particulates with the release of puffs, particles, or a combination of both, which is user specified.

The dispersion rate is calculated from the vertical diffusivity profile, wind shear, and horizontal deformation of the wind field. Air concentrations are calculated at a specific grid point for puffs and as cell-average concentrations for particles (Draxler and Hess, 1998). One of three assumptions can be used to compute air concentrations along the parcels trajectories, a puff model, a particle model or a combination of puff and particle models called PARTPUF. The combination method was used in this study.

Options in HYSPLIT_4 allows for gravitational settling, wet and dry deposition and re-suspension of pollutants Draxler and Hess (1998). These options give more flexibility to replicate realistic conditions and allow for various tests. This model has been under development since 1982. The accuracy of trajectories and dispersion/deposition using numerical model output has been tested using data collected during several field experiments. Results indicate that no discernible differences were seen with the average error rates in the 20% to 30% range of the travel distance. These results indicate that model output can be used for the meteorological fields for trajectory models. These studies indicate that the use of trajectory models from the use of numerical forecast models, even ones with relatively large grid sizes and time steps, have results that have utility in this study.

Although SBR spores can be transported over great distances, they may not be viable once they are deposited. Spore viability is dependent on four criteria; 1) time, 2) UV-B exposure, 3) temperature and 4) precipitation. The SBR spore concentrations over time were decimated by each of these factors. To decimate the SBR spore concentrations over time, we have assumed an exponential decay, similar to radioactive decay, to reduce the number of viable spores with time. Although SBR spore viability does not typically follow a radioactive decay profile, we do not know how long each spore has been aloft so an exponential decay for all of spores suspended has been assumed.

It is known that SBR spore viability decrease rapidly when the ambient temperatures are sub-zero for more than seven days. Since the source regions for of the SBR spores are in the tropics, the 0° C temperature is about 3-4 km above the ground surface. Only those spores above 3 km above were decimated over the total duration for which the spores were suspended.

SBR spore viability is also affected by exposure to UV-B radiation. Unfortunately determining the amount of UV-B exposure is a complex since exposure is affected by the amount of cloud cover of the current location and the amount of ice coating if any. We have assumed to have an e-folding time at 60 MJ day^{-1} total radiation, of which about 30 MJ per day is in UV portion.

In order to inoculate a soybean plant, the SBR spores require moisture. Precipitation washout of the SBR spore provides a means of removing the SBR spores from the air and provides the necessary moisture needed by the spores. We adopted half-time wet deposition of 25 mm precipitation (Isard *et al.*; 2003).

We use pathway frequency as a measure of the probability that an area or region is suspetibale to infection of SBR spores.-It should be pointed out that the maximum likelihood pathway frequencies are computed only from trajectories, thus do not represent actual spore concentrations, but are related to source regions. The pathway frequency can be interpreted as a region where SBR infections could occur.

Results

Experiments with the coupled for SBR forecasting began in 2003 with the creation of maximum likelihood pathway frequency maps, similar to those produced by Isard et al. (2003). These pathway frequency maps indicated that there were only a few pathways to the southern United States. The forecasts of SBR concentrations over our domain of interest also indicated that it was unlikely that SBR would arrive in the Continental United States in 2003.

The same series of experiments were conducted during the summer of 2004. These new experiments indicated a different scenario for the late summer and early fall of 2004. As with the previous year two prediction experiments were carried out: one creating the maximum likely hood pathway frequency maps, and the second creating the concentration maps. Further, these forecast experiments were carried for two 40-day periods, one starting early August and the other in early September. The first forecast period was begun after the detection of SBR in Cali and the second one corresponding to the middle of hurricane season.

Figure 2a shows the prediction of spore pathway as represented by the high frequency of pathway beginning on August 7, 2004 and ending on September 17, 2004. As noted earlier the ECPC's GCM provided the boundary whereas MM5 provided the meteorological forecasts over the forecast region. Within MM5 a two-way interactive nesting is also employed, which means the information in coarse and fine MM5 domains are free to interact with each other, which results in better meteorological simulations.

The source points of spores were placed in 2.0^o x 2.0^o rectangular area centered at Cali (Fig. 2). The source points were uniformly distributed at 90 grid points separated by 0.05^o of latitude and longitude. The source is assumed to release spores continuously during the integration and the spores can reach at least 10 m above the ground by turbulence. The majority of spores released from the sources moved westward to the Pacific Ocean following the easterly winds. These spores turned north later but did not reach the northern Mexico or United States.

The first maximum likelihood pathway frequency forecast was conducted without any environmental limitation on the spore viability. In this experiment, the spores were treated as markers on air parcel trajectories. The spore clouds mainly moved northward in large amounts across southern and eastern Mexico and the Gulf of Mexico and finally reached the continental U.S. The high frequency areas cover south and eastern Texas, Louisiana, and moderate frequency in Georgia, and Florida (see Fig 2a). This would suggest the disease in Texas where no rust was detected so far. Although the dry weather during the time period could have prevent the disease. The second maximum likelihood pathway frequency forecast included UV-B decimation and a 10-day life span. This limitation mimics the temperature effect on spore viability. Incorporating UV-B decimation and a ten-day lifetime results in a sharply reduced maximum likelihood pathway frequency (Fig. 2b). Only two distinct strands of spores moved northward directly towards the U.S. One started from the southern tip of Gulf of Mexico along east coast of Mexico and finally reached Louisiana, U.S. where the first detection of the rust and most widely spread among all five states occurred. The pathway matches closely the detected locations of the rust shown in Fig. 1. This strand also resembles the track of Hurricane Bonnie that developed over the Gulf of Mexico during August 9-12, 2004 although the model predicted track is somewhat east of the observed. The reason can be that the storm developed from the ocean sheltered the rust spores from UV radiation. The spores in the storm-free areas were killed after enough radiation exposure. The other strand directly extends from Cali to Georgia and Florida. It's frequency is lower the western one, in agreement with relatively less widespread of the rust in these two states. This strand again is associated with the cloudiness of a storm, most likely Hurricane Ivan.

The distinct strand structure when UV radiation is considered strongly suggests the key importance of UV radiation as a criterion for the spore viability. The correlation between hurricane tracks and spore pathways provides further evidence that clouds in a storm system protect spores from UV radiation.

Nevertheless the diagnosis of the single release of the spores showed the western strand occurred in early August may be responsible for the rust in Louisiana, and neighboring states and while the eastern one in early September is responsible for the disease in Georgia and Florida. The early one was likely associated with Hurricane Bonnie while the late one was likely related to Hurricane Ivan. It should be noted that the accurate timing does not have significant meaning for single events in the framework of seasonal or long-term prediction. This probably explains why the time difference in the two strands (~one month) does not correspond the time difference in disease occurrence among states.

A second forecast was begun on September 4, again for 40-days, ending before the first detection of the disease. This forecast also showed a clear preferred pathway towards the Louisiana, suggesting that this pathway is the most likely route. Based on this forecast the air parcels first moved from the Cali region and then move northeast into Ivan system following the track of the cyclone to the United States.

Although the maximum likelihood pathway frequency forecasts provide an indication of SBR contamination, these forecasts do not account for dispersion, deposition washout and other factors that would alter the number of SBR spores in an air parcel. Indeed the maximum likelihood pathway frequency forecasts merely indicated the number of air parcels that may contain SBR spores that have passed over a particular point in space. A more accurate approach is to determine the actual SBR spore concentration from the SBR spore emission rates and a dispersion/deposition model. NOAA's HYSPLIT_4 modeling system for trajectories, dispersion and deposition was again combined with NCAR's MM5 to produce forecasts of SBR spore concentrations except HYSPLIT-4 was run in concentration mode rather than trajectory mode. Source regions for SBR spores in Brazil and Columbia were obtained from Yang *et al.* (200X). Each source region occupied the full area of the grid square and an emission rate of 3.619×10^{12} spores per hectare per hour (Isard, *et al;* 2003). The number of spores deposited on the surface and spore concentrations at 5, 10, 100, 500, 1000 and 5000 meters above ground level (AGL) were computed over the 40-day period. As with the maximum likelihood pathway frequency forecasts UV-B decimation and a 10-day life span in the air is imposed on the spores.

Unlike the maximum likelihood pathway frequency chart shown in Fig. 2, the concentration forecasts are created every 3 hours at each of the seven levels. The resulting concentrations are plotted to determine the areas in the forecast domain affected by SBR spores. The resulting concentration maps allow the changes in concentrations change over time. A single concentration map does not describe the detail shown in an animation of the same region. Time-lapse movies of the concentrations at each of the seven layers for the 40-day period are available at http://www.eas.slu.edu/People/RWPasken/sbr/movies. These time-lapse movies clearly demonstrate that the SBR migrated from Brazil and Columbia into the United States as each of the hurricanes passed from the Atlantic to Gulf of Mexico and finally the southern Gulf Coast. Figure 3a is the number of soybean rust spores deposited per square meter on the for 06 UTC on August 11, 2004. Fig 3a shows that the SBR spores are concentrated in South America and along the Inter-Tropical Convergence Zone (ITCZ) on the west side of Central America. By 21 UTC on August 11, 2004 a strand of SBR spores from Columbia and Brazil has stretched to Haiti and the Dominican Republic. The SBR spore concentrations for 12 UTC August 15, 2004 (Fig. 3c) mark Hurricane Francis's landfall over southern Florida. The simulation indicated that as Francis makes landfall approximately 100 SBR spores per square meter were deposited over most of Florida. The Gulf Coasts of Louisiana, Mississippi, Georgia and Alabama indicates surface depositions of 1 to 5 SBR spores per square meter. It is important to note that figure show the number of spores deposited on the surface over a 3-hour period. The total accumulation over the lifetime of the event would be higher.

The importance of the fine-scale structure of the atmosphere in controlling the dispersion and deposition of SBR spores is revealed in the vertical distribution of SBR spores (Fig. 4). The atmospheric boundary layer is typically 1 km deep, while over 70% of the SBR spores were trapped below 4 km AGL. Although the Fig. 4 shows the SBR spores initially trapped below 1 km AGL and deepens over time to 4 km, the increase in depth is an artifact of the initial launch of the SBR spores at the beginning of the forecast. This is because the model starts with an atmosphere void of any spores. In reality, the SBR spores were already present throughout the 4 km deep column near the end of the forecast period. The shallow depth over which the SBR spores are spread suggests that the determining factor for the dispersion and deposition of the spores would appear to be the depth of the boundary layer and vertical dispersion and transport in the small-scale flow.

Heavy precipitation associated with the hurricanes is indicator of the importance of the small-scale and boundary layer flow. Wet deposition of SBR spores promotes inoculation of rust (Yang *et al.*; 1991, Yang *et al*; 1990). For example, the heavy rainfall center close to the eye wall of Ivan (to a lesser degree, Bonnie) coincides with the region where fields infected with SBR were found. This result strongly suggests the rainfall washout played a key role during the event. The heavy rainfall washed out the airborne spores and provided moisture for the subsequent disease to develop (Tan *et al*; 1996). Rainfall amount and rain frequency are very important determinants for the disease epidemics (Yang *et al.,* 1990). In contrast, the lack of rainfall in Texas provides an explanation for the lack of SBR infection, although the minimal number of hosts in this region may be partly responsible also. Even if -SBR spores present, there are no mechanisms to deposit them to the ground and the lack of moisture would inhibit their survival, and increase the UV-B radiation which would make the viability of SBR spores difficult.

If the small-scale flow were the only determining factor, the SBR spores could not be carried over large distances. If, however, the large-scale flow were also a controlling factor then the structure of the ITCZ would control the spread of the SBR spores. Typically the ITCZ would carry the spores to the Pacific Ocean. Strong meridional flows are associated with numerous strong hurricanes disrupted the climatological zonal flow, permitting air parcels to move across the weakened ITCZ. This is seen by eight named hurricanes occurring in August, a record (Shinngle; 2004). Fig. 5 is the streamlines at 850 hPa during the period of hurricane Ivan. The streamlines show a strong southerly flow from the Cali region to hurricane tracks. This meridional flow was quite persistent during much of the hurricane season including the time of Bonnie. Thus, this bridging flow carried spores to the hurricanes which transported them to the continental United States. This strong bridging flow implies that the large-scale flow is a major contributing factor in determining the dispersion and deposition of SBR spores. The streamline field in Fig. 6 further demonstrates that movement of SBR spores is controlled by the large-scale structure of the atmosphere. Fig. 6a reveals the classical climatological zonal flow and the transport of SBR spores by the large-scale flow towards the ITCZ and then over the Pacific Ocean. Zonal flow breaks down with the approach of the hurricanes, the zonal flow breaks down and becomes meridional. This allows the SBR spores from both Brazil and Columbia to be drawn into the air entering the hurricane (Fig. 6b).

Discussion

The primary factor controlling the prediction of the arrival of SBR spores in the United States is the quality of the meteorological forecasts. Although the meteorological models predict the arrival of the hurricanes along the Gulf Coast, the timing and location of the landfall of these hurricanes were incorrect by as much as a day. For our purposes, a forecast error as large as this large is not as important as correctly predicting the occurrence of the hurricanes. Coated with water and shielded from UV radiation by the hurricanes extensive cloud deck the SBR spores are able to survive longer than would otherwise be possible. As the hurricanes passed into the Gulf of Mexico air was drawn from Brazil and Columbia into the hurricanes core. As the hurricanes makes landfall the SBR spores are washed out of the air and onto host plants. The SBR spores act as cloud condensation nuclei (CCN) and become coated with water. Since the spores are coated with water and embedded with the deep cloud cover associated with the hurricane, the spores are protected from the UV that would normally kill them. When the SBR spores are washed out as the hurricanes make landfall (Fig 6c), the water-coated SBR spores have a ready source of the moisture needed to germinate enhancing the risk of SBR infection. Thus, spores drawn into hurricanes have an enhanced probability of infecting hosts

Detailed verification of these forecasts is limited by the lack of measured atmospheric SBR spore concentrations in the continental United States, however, the detailed verification of the methodology by Pasken and Pietrowicz (2005) indicates that it is sound. To further test the methodology, concentration forecasts were recreated using observed data over the same period rather than forecasts in November 2005. These new concentration forecasts remove the meteorological forecast dependency and leave only a dependency on the quality of the dispersion modeling. These new concentration forecasts differed only in the timing of arrival of the SBR spores, suggesting that the meteorological forecast plays a major role in the dispersion and deposition of SBR spores. This is consistent with results discussed in Pasken and

Pietrowicz (2005). In addition, the lack of measured concentrations does not prevent a verification of the maximum likelihood pathway frequency and concentration forecasts in a subjective manner. The success of the long-range meteorological forecasts and the consistency of the maximum likelihood pathway frequency and concentration forecasts predicted the arrival of SBR in the United States in late August and early September. Given the time needed for germination and the time needed to verify the infection, SBR spores would have needed to arrive in the same time frame. These forecasts can be further confirmed by the presence of SBR infections in areas where the highest forecasted SBR spore concentrations and largest maximum likelihood pathway frequency values intersect.

Conclusions

Forecasting the arrival Phakopsora Pachyrhizi in the United States is an extremely complex problem, because it requires meteorological forecasts at several scales of atmospheric motion over an extended period, a dispersion/deposition forecast and an understanding of plant pathology. We have shown that it is possible to make a forecast of the dispersion and deposition of plant pathogens over a long period with reasonable accuracy, as indicated by the location of SBR infections and the correlations of deposition and maximum likelihood pathways.

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Figures

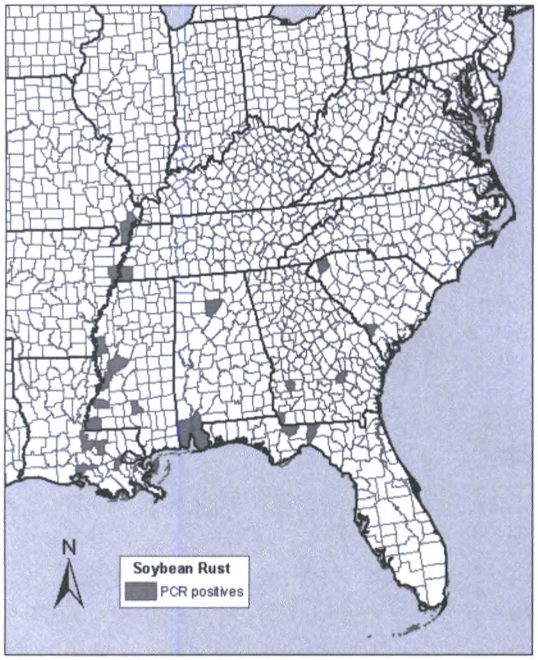


Figure 1. Sites of soybean rust detected in November 2004. https://netfiles.uiuc.edu/ariatti/www/SBR/USmap.html

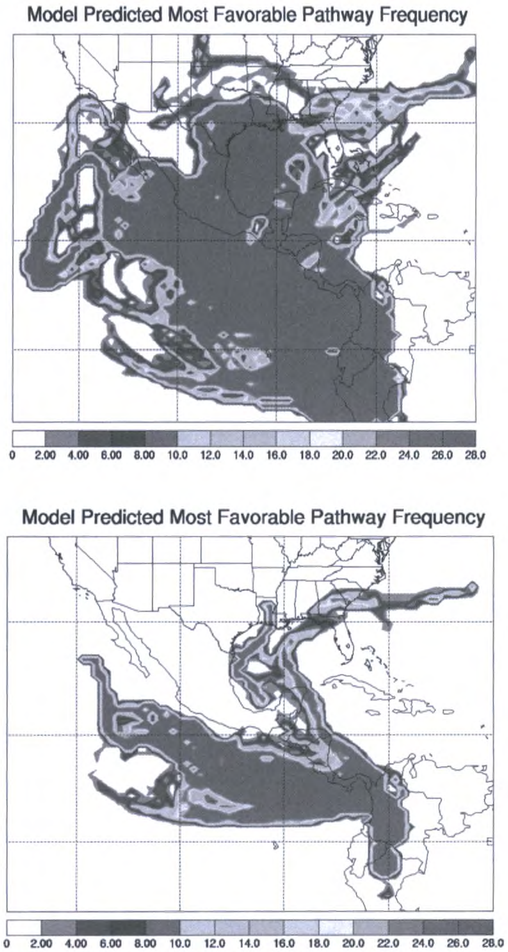
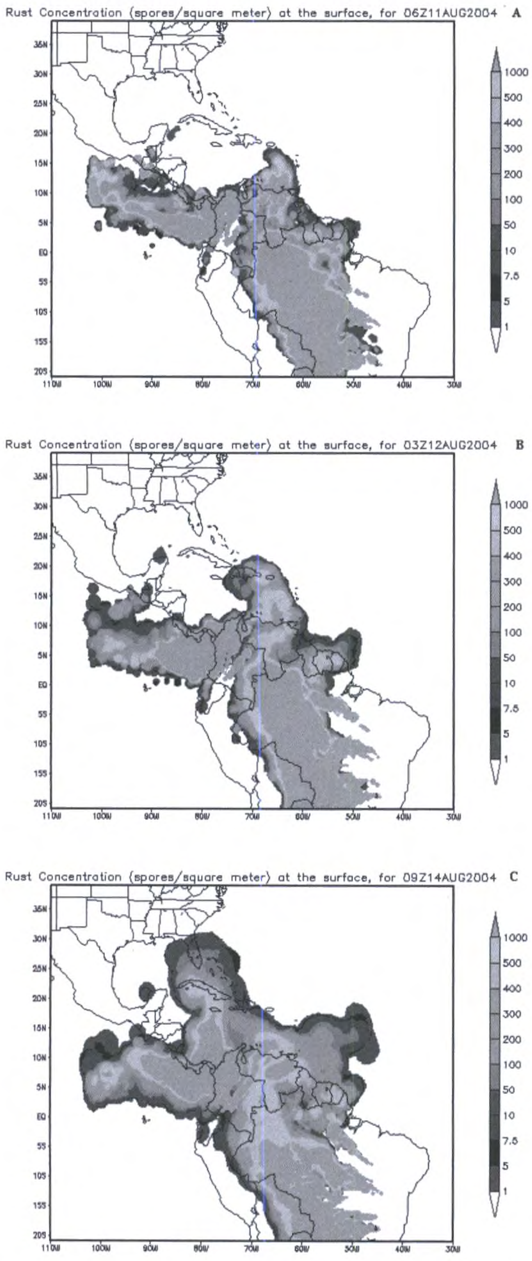


Figure 2. Predicted most preferred pathway of soybean migration. (a): With no limitation on soybean rust viability; (b) With UV radiation and maximum life time span.

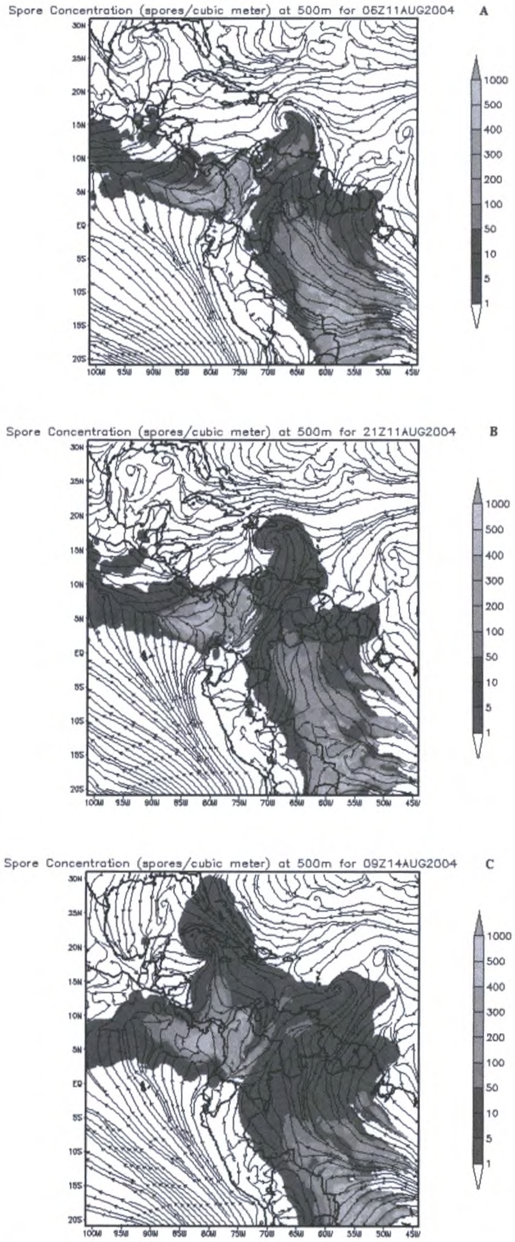


Rust Concentration (spores/square meter) at the surface, for 06Z11AUG2004 A

Rust Concentration (spores/square meter) at the surface, for 03Z12AUG2004 B

Rust Concentration (spores/square meter) at the surface, for 09Z14AUG2004 C

Figure 3. Soybean rust spore deposited on the surface and 10m streamlines for (a) 6 UTC August 11, 2004 (b) 3 UTC August 12, 2004 and (c) 9 UTC August 14, 2004



Spore Concentration (spores/cubic meter) at 500m for 06Z11AUG2004 A

Spore Concentration (spores/cubic meter) at 500m for 21Z11AUG2004 B

Spore Concentration (spores/cubic meter) at 500m for 09Z14AUG2004 C

Figure 6. Soybean rust spore concentrations and 500 m streamlines for (a) 6 UTC August 11, 2004 (b) 21 UTC August 11, 2004 and (c) 12 UTC August 15, 2004

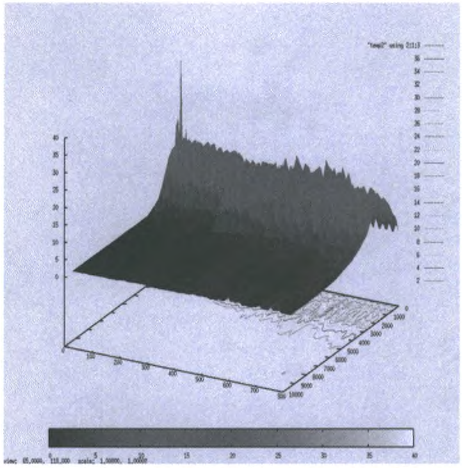


Figure 4. SBR concentration versus time and altitude

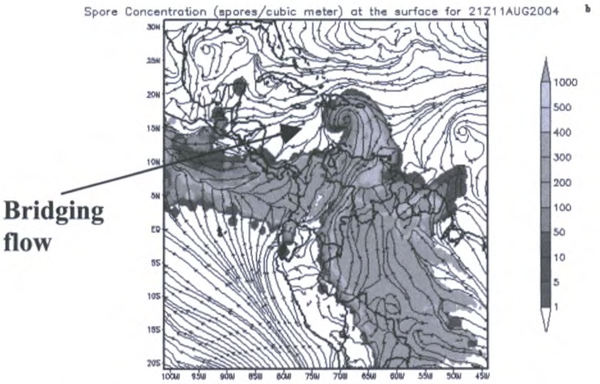


Figure 5. Streamline flow for 21 UTC August 11, 2004 showing the meridional flow from Columbia to the Gulf of Mexico

Ammonia Volatilization During and Following Dairy Slurry Application in the Field

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Abstract

Livestock manure is known to be a major source of atmospheric ammonia (NH_3). In order to determine the magnitude of these emissions, daytime ammonia fluxes were measured following the application of dairy slurry in a forage field using two micrometeorological approaches. The Relaxed Eddy Accumulation technique and the Flux Gradient technique were used in conjunction with denuder tube coated with oxalic acid as a trapping medium. The flow rate was set at 2 L min^{-1}. The 60-cm long denuder tubes were extracted with 3 - 10 mL of deionized water. The NH_4^+ concentration in water was analyzed with an ion chromatograph (Dionex DX-600 System) equipped with a ED50 Electrochemical Detector and using a Dionex CS-16 analytical column, guard column and 38 mM MSA as the eluent at ambient temperature. The detection limit of NH_4^+-N concentration was 0.24 μg L^{-1}. The rate of application of the dairy slurry was 83 kg N ha^{-1}. The highest NH_3 emissions occurred on the first day after application with maximum ranging between 11-13 μg N m^{-2} s^{-1}. The ammonia volatilization was reduced by 6 - 7 fold on the second day and was in the range of 1-2 μg N m^{-2} s^{-1}. By the third day, NH_3 fluxes were one order of magnitude lower than the second day. Over 11 days of observation, 1.5 kg NH_3-N ha^{-1} was volatilized during the daytime, which is less than 2% of the total slurry amount applied. Almost two third of the NH_3 emissions occurred on the first day. Under these conditions of limited ammonia volatilization, both methods gave consistent results and were able to detect small fluxes. These data will be used to verify process-based models.

Exploration and Application of Statistical Methods to Identify Vegetation-Surface-Atmospheric Interactions Using Field Observations

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Abstract

Vegetation affects the surface energy balance and the associated winds and regional circulation patterns. Efforts are underway to understand the magnitude and nature of the different variables that can participate in the land surface – atmosphere processes. There is also considerable variability and uncertainty associated with the specification of vegetation-soil-atmospheric parameters in environmental models. The main objective of this study is to apply statistical methods to identify significant interactions between vegetation, land-surface and atmospheric factors and their effects on latent heat flux in non urban areas. Three different statistical techniques such as (i) a resolution IV fractional factorial (FF) design based approach; (ii) the fractional factor separation (FFS) approach and a generalized least square (GLS) regression method have been used to conduct the analysis. The results from the three different methods are analyzed using data from the ten field stations from the International H_2O project (IHOP 2002). Significant variability exists between the different stations due to their spatial location, vegetation, availability of soil moisture. The questions this study seeks to answer are (i) how do the three different statistical methods compare in terms of capturing the interaction patterns, and (ii) whether the complete and continuous structure of the explanatory variables provide better information than the partially grouped data? It was found that in all the 10 stations, the fractional factorial methods and Factor Separation methods yielded very similar results and confirmed the presence of at least two way interactions. However higher order interactions were difficult to identify due to the confounding of effects and absence of several combinations. This feature, i.e. inability to always the best combinations of variables settings to extract the different interactions, remains a limitation of the current analysis, which can be reduced in future studies by considering the interaction considerations in designing the field experiments. Multivariate visualization display further confirmed that utilizing continuous information as compared to discrete combinations can better capture the patterns and help explain the large variability present. There were indication that GLS procedure is also useful in terms of detecting higher order interactions and non linear relationships between the factors which were undetectable by both FF and FS methods. The shortcomings of the three approaches are addressed and the trade off between using these approaches is discussed.

Recovery of Malodorous Livestock Odors and Gases from Tedlar® Sampling Bags Using Olfactometry and Thermal Desorption Tubes

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Abstract

Analysis of odors with attention to improving air quality is of great interest to agricultural communities; therefore it is important that odor samples are representative of conditions at the time of sampling. The purpose of this research was to quantify the recovery of odor and odorous chemicals in commercial and homemade Tedlar® sampling bags. A standard gas generator was used to produce a standard gas mixture consisting of seven volatile fatty acids: acetic (941 ppbv), propionic (5212 ppbv), isobutyric (468 ppbv), butyric (291 ppbv), isovaleric (296 ppbv), valeric (154 ppbv), and hexanoic (454 ppbv) acids and one semi-volatile organic compound, para-cresol (9 ppbv). The standard gas was placed in the Tedlar® bags and chemical concentrations were quantified at times of one hour, one day, two days, three days, and seven days using thermal desorption tubes and a gas chromatograph/mass spectrometer (GC/MS). Odor concentration, intensity, and hedonic tone were measured by human panelists using dynamic triangular, forced-choice olfactometry.

Chemical recoveries ranged from 2 - 40% one hour after sampling and 0 - 14% after seven days, an indication that chemical concentrations decreased with time in the bags. Odor concentrations in Tedlar® bags as observed by olfactometry panelists decreased approximately 8% after one day and 14-39% after seven days. Minimal changes were observed in intensity and hedonic tone. These results suggest that Tedlar® bags influence gas concentrations with some potential to affect odor. Appropriate precautions should be taken in the selection of odor sampling bags to avoid contamination or non-representative analyses. It is apparent that bag samples will experience considerable reductions in chemical concentrations immediately upon collection. Minimizing time between the sampling event and sample analysis is still important in reducing overall chemical losses.

Introduction

Air quality is of great interest to agricultural communities. It is therefore important that odor samples are representative of the conditions sampled when testing the quality and quantity of odor experienced in these communities. Tedlar® sampling bags are used by many because of its low cost, low permeability, and non-reactive, chemically inert qualities (Parker et al., 2003). In olfactometry analysis, odor samples are presented to a group of panelists to determine detection threshold (DT), intensity, and hedonic tone.

Zhang et al. (2001) found a poor correlation between intensity measured in the field with Nasal Rangers and odor concentration measured with Tedlar® sample bags and olfactometry. However, the odor intensity of bagged samples did correlate well with the olfactometry measurements. Parker et al. (2003) found background DTs to increase with increased holding time in Tedlar® bags and considered heating at 100^{o}C as well as purging after heating and again prior to sampling necessary to reduce background DTs to an acceptable level. Williams (2003) considered Tedlar® bags able to remove organic acids from swine odor samples unless samples were analyzed within a few hours of collection. Keener et al. (2002) also found that Tedlar® sampling bags had background odorants that affected olfactory analysis of samples. In Keener's study, tri-packed sorbent tubes (Tenax TA, Carboxen 1000, and Carbosieve SIII) were able to recover greater than 74% of the 19 swine odorants tested.

According to Spinherne et al. (2003), volatile fatty acids (VFAs) are considered important components of agricultural, solid waste processing and disposal, industrial and municipal wastewater collection, and treatment system odors. Spinhirne developed a standard gas mixture which consisted of acetic, propionic, isobutyric, butyric, isovaleric, valeric, and hexanoic acids and was considered representative of agricultural odors using a gas generator and permeation tubes (Spinherne et al., 2003). Koziel et al. (2004) compared recoveries using a standard gas mixture with SPME fibers and Tedlar, FEP (Teflon), foil, and PET (Melinex) sampling bags. The standard gas mixture used in Koziel's study included acetic acid, propionic acid, isobutyric acid, butyric acid, isovaleric acid, valeric acid, hexanoic acid, p-cresol, 2'-

aminoacetophenone, indole, and 4-ethylphenol. The SPME fibers were identified with the highest recoveries (106.2% and 98.3%), followed by the PET (71.7% and 47.2%), FEP (75.4% and 39.4%), homemade Tedlar® (47.3% and 37.4%), commercial Tedlar® (67.6% and 22.7%), and foil (16.4% and 4.3%) bags. Recoveries were greater at the 0.5 hour storage time as compared to the 24 hour storage time (Koziel et al., 2004). Koziel et al. (2005) used Tenax TA sorbent tubes with the standard gas mixture and found them able to recover 94.8% at the 0.5 hour and 88.3% at 24 hours storage time, realizing the second greatest recoveries when compared to the previous SPME and bag tests.

The objectives of this research were to quantify the recovery of odor and odorous compounds in Tedlar® sampling bags at times of 1 hr to 7 days using a standard gas mixture and GC/MS analysis.

Materials & Methods

Two types of 10L Tedlar® bags were considered in this study, a commercial Tedlar® (SKC Inc., 863 Valley View Road, Eighty Four, PA 15330) and the WTAMU homemade Tedlar® (constructed with Dupont^{TM} TST20SG4 transparent film, baked at 100°C for 24 hours per Parker et al. (2003)). A standard gas mixture consisting of acetic acid, propionic acid, isobutyric acid, butyric acid, isovaleric acid, valeric acid, hexanoic acid, and p-cresol was used in these trials. Bags were filled with the standard gas mixture seven, three, two, and one day prior to olfactometry testing. On the day of olfactometry testing, a one hour standard gas sample was obtained as well as an odor-free (Zero-Air) air sample in the bag type to be tested that day. This scenario was used for both bag types.

Thermal desorption tube samples (Tenax TA) were obtained from each bag by passing 600 ml of gas through the tube using an SKC Pocket Pump (SKC Inc., Eighty Four, PA 15330). Thermal desorption tube samples were also obtained directly from the standard gas generator to quantify the concentrations of the standard gas.

All tube samples were analyzed using a Perkin-Elmer automated thermal desorber (ATD) (710 Bridgeport Avenue, Shelton CT 06484-4794) and a Varian 3800/Saturn 2000 gas chromatatraph (GC) equipped with a mass spectrometer (MS) (Varian Inc., Walnut Creek, CA 94598). Samples were automatically desorbed and injected into the GC/MS. Upon injection, samples were held at 250°C for 20 minutes in the splitless mode with a 1 mL/min flow of helium. The column oven began at 60°C and increased to 230°C at a rate of 6°C per minute for a total run time of 30.3 minutes. The strongest ion, quan ion, and other ions as molecularly described by the NIST database were used in the method for accurate identification of each compound. The GC/MS compares the area of each peak in the sample tested to associated peaks in the standard samples used to develop the method, calculating concentration in parts per billion.

Olfactometry analysis was performed at the WTAMU Olfactometry Lab per ASTM Standards (ASTM, 2001a, b, c) on day-7 of each experiment, analyzing odor in sample bags that had been maintained at room temperature for 1-hr, 1-day, 2-days, 3-days, and 7-days. All potential panelists were previously trained in all aspects of the odor analysis. Panelists were selected based on sensitivity to an n-butanol reference gas sample as described in the ASTM standards. Panelists identified with adequate sensitivity that day were eligible for the panel. Those individuals considered hypernosmic or anosmic were excluded. The panel was conducted with four panelists sniffing each sample twice, yielding a total of eight readings per sample. A machine blank was obtained and analyzed before beginning analysis of the actual odor samples.

Samples were analyzed for odor concentration (detection threshold, DT) using a triangular forced-choice olfactometer (AC'SCENT International Olfactometer, St. Croix Sensory, Inc., Lake Elmo, MN). Individual panelist DTs were calculated according to ASTM standards (2001b) as the geometric mean of the concentration at which the last incorrect guess occurred and the next higher concentration where the odor was correctly detected. Samples were analyzed for intensity using a static-scale method by comparison to five standard n-butanol solutions, following the general guidelines of ASTM (2001a). Solutions consisted of 0.25, 0.75, 2.25, 6.75, and 20.25 ml n-butanol per L of water, which corresponded to intensities of 1.0, 2.0, 3.0, 4.0, and 5.0, respectively. Intensity scores ranged from 0.5 for an odor sample weaker than the lowest n-butanol concentration to 5.5 for an odor stronger than the highest concentration, in increments of 0.5. The average intensity was calculated for the panel using the arithmetic mean. Hedonic tone (HT) was determined in a similar manner by sniffing the full strength odor sample. Panelists were asked to subjectively assign a score for hedonic tone on a scale of -4 to +4, with -4 being very unpleasant, 0 being neutral, and +4 being very pleasant. The average hedonic tone was calculated for the panel using the arithmetic mean.

Concentrations for both the commercial and the homemade Tedlar® bag types were obtained in the GC/MS chemical quantification analyses. Percent recoveries of chemical compounds were calculated as the amount recovered at time T divided by the concentration of the standard gas on the day that bag was sampled. In the olfactometry data, percentage decrease in the panel detection threshold (PDT) was calculated by dividing the PDT of the 1, 2, 3, and 7 day samples by the PDT of the 1-hour samples.

Results

Detectable concentrations of all eight compounds were detected in the Zero-Air samples for both bag types (Table 1). This indicates that Tedlar® bags have the potential to affect odor analyses of agricultural odors as sampled.

Table 1. Background Chemical Concentrations in Homemade and Commercial Tedlar® Bags.

Zero-Air Samples	**Homemade Tedlar®** ***Conc. (ppb)***	**Commercial Tedlar®** ***Conc. (ppb)***
Acetic Acid	82.53	29.956
Propionic Acid	118.906	119.148
Isobutyric Acid	4.626	15.444
Butyric Acid	3.074	5.104
Isovaleric Acid	1.256	4.218
Valeric Acid	1.123	1.093
Hexanoic Acid	10.66	7.075
P-cresol	0.142	0.179

Chemical concentrations found in the bags, and therefore percent recoveries, were greater for the 1 hour samples than the 1, 2, 3, or 7 day samples for both types of Tedlar® sampling bags. Recoveries ranged from 2.4% to 40.1% for the 1-hour samples and from 0.2% to 19.8% for the 7-day samples (Tables 2 & 3).

Table 2. Concentrations and Recoveries in Homemade Tedlar® Bags

WTAMU Homemade Tedlar®	*1-hour Conc. (ppb)*	*1-hour % Recovery*	*1-day Conc. (ppb)*	*1-day % Recovery*	*2-day Conc. (ppb)*	*2-day % Recovery*	*3-day Conc. (ppb)*	*3-day % Recovery*	*7-day Conc. (ppb)*	*7-day % Recovery*
Acetic Acid	303.971	19.0%	162.228	13.5%	100.828	10.6%	78.846	8.1%	36.487	6.4%
Propionic Acid	1463.095	21.5%	757.905	12.6%	552.680	10.0%	494.662	8.1%	90.912	1.4%
Isobutyric Acid	218.211	38.4%	183.858	34.3%	143.669	29.3%	139.068	25.3%	28.991	5.4%
Butyric Acid	64.848	17.9%	38.648	11.7%	26.160	8.0%	21.149	6.2%	3.180	1.0%
Isovaleric Acid	94.033	27.0%	62.3	18.0%	45.909	13.9%	42.087	12.0%	0.958	0.3%
Valeric Acid	8.667	4.7%	5.674	3.3%	3.387	1.9%	2.663	1.5%	0.511	0.3%
Hexanoic Acid	86.388	14.5%	42.54	9.7%	29.003	4.9%	23.252	8.2%	4.061	2.6%
P-cresol	0.264	2.4%	0.163	1.6%	0.166	1.3%	0.162	1.5%	0.000	0.0%

Table 3. Concentrations and Recoveries in Commercial Tedlar® Bags

SKC Commercial Tedlar®	*1-hour Conc. (ppb)*	*1-hour % Recovery*	*1-day Conc. (ppb)*	*1-day % Recovery*	*2-day Conc. (ppb)*	*2-day % Recovery*	*3-day Conc. (ppb)*	*3-day % Recovery*	*7-day Conc. (ppb)*	*7-day % Recovery*
Acetic Acid	97.085	14.2%	91.388	9.4%	70.887	8.5%	102.389	12.7%	116.723	14.1%
Propionic Acid	673.731	19.4%	548.008	13.7%	401.134	9.2%	444.378	10.3%	215.662	4.3%
Isobutyric Acid	140.718	40.1%	141.399	35.6%	125.299	33.0%	125.958	31.1%	53.502	11.3%
Butyric Acid	38.294	18.6%	29.696	12.4%	21.832	8.6%	20.326	8.0%	5.711	2.0%
Isovaleric Acid	57.771	27.7%	48.226	20.2%	34.025	13.5%	32.918	12.7%	4.324	1.5%
Valeric Acid	5.463	4.9%	3.064	2.3%	2.363	1.8%	2.255	1.6%	0.331	0.2%
Hexanoic Acid	14.297	3.7%	15.621	2.4%	6.907	1.4%	10.062	2.1%	2.544	0.5%
P-cresol	0.251	4.5%	0.273	3.9%	0.161	2.2%	0.268	3.9%	0.312	4.9%

This data indicates a portion of the chemical compounds present in air sampled with Tedlar® bags would not be available to the panelists upon olfactometry analysis, the amount depending on the length of time in the bag endured between sampling and analysis.

Olfactometry analysis indicated little difference in panel detection threshold (PDT), intensity, or hedonic tone between the homemade and commercial Tedlar® varieties (Table 4). Background odor (zero air in Table 4) was detected by the panelists in both varieties, with a greater PDT (stronger odor) in the commercial Tedlar®. Samples experienced a reduction in odor (PDT) with no great change in hedonic tone or intensity relative to time in the homemade Tedlar® bags. Air samples in the commercial Tedlar® bags however experienced a slight increase then a decrease in PDT with time, and again no great changes were apparent in hedonic tone or intensity. Percent reductions show an 8 % loss in odor in the first 24 hours (1-day) and a 14-39% loss in 7 days.

It should be noted that while we were able to determine the concentration of the chemical compounds in the standard gas, we did not directly measure the PDT of the standard gas because the gas had to be placed in the Tedlar® bags for olfactometry analysis. For this reason, the percent recoveries in the olfactometry analysis were calculated relative to the 1-hour sample. Thus, a direct comparison of the percent recoveries between the chemical concentrations (Tables 2 & 3) and the olfactometry data (Table 4) is not valid.

Table 4. Olfactometry data for both the homemade and commercial Tedlar® varieties.

	PDT	**% Recovery**	**Intensity**	**Hedonic Tone (4)**
Homemade Tedlar				
Zero Air	8		0.8	0.0
1 Hour	323		3.1	-2.5
1 Day	296	92%	3.1	-2.3
2 Day	271	84%	3.5	-2.5
3 Day	232	72%	3.3	-2.5
7 Day	196	61%	3.3	-2.5
Commercial Tedlar				
Zero Air	19		1.8	-0.8
1 Hour	191		2.8	-2.0
1 Day	298	92%	3.1	-2.0
2 Day	401	124%	2.1	-2.0
3 Day	401	124%	2.5	-2.0
7 Day	277	86%	2.3	-1.8

Conclusions

The chemical compounds present in the standard gas could not be completely recovered once placed into either commercial or homemade Tedlar® sampling bags. The time spent in the bags affected odor as perceived by olfactometry panelists, as would be expected from the reduced recoveries of chemical components. Therefore, Tedlar® bags may not be the best sampling device for maintaining chemical integrity of air samples for odor analysis. Other methods of air sampling may provide a more chemically complete sample for analysis.

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Spatial Variability of Emissions from Swine Confinement Operations

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Abstract

Over the past five years the interest in gaseous emissions from animal confinement operations has increased rapidly. The increase in the size of the facilities as well as the geographic concentration of facilities has led to serious concerns regarding adverse health affects on workers and the surrounding population. Attempts to regulate the emissions by state and federal agencies have been hampered by the complexity of the required analyses and variability of emission factors found in the literature. Because of this variability, it is very difficult to make measurements that reflect the overall emissions from the facilities.

Ammonia concentrations around facilities range from less than 10 ppbv to 100 ppmv depending on factors such as season, wind speed, wind direction and distance away from the facilities. The type of storage lagoon such as covered verses uncovered affects the concentrations of gases such as ammonia, methane and hydrogen sulfide. Daily average ammonia and hydrogen sulfide concentrations were 805 ppbv and 25 ppbv, respectively over an open lagoon and the daily average methane concentration was 24 ppmv over a covered lagoon. The choice of sampling height, location of the sampler, and season also affected the concentrations measured. Some sort of "standard protocol" must be established before emission rates can to determined and applied to swine confinement operations.

Introduction

Over the past five years the interest in gaseous emissions from animal confinement operations has increased rapidly. The increase in the size of the facilities as well as the geographic concentration of facilities has led to serious concerns regarding adverse health affects on workers and the surrounding population. Attempts to regulate the emissions by state and federal agencies have been hampered by the complexity of the required analyses and variability of emission factors found in the literature (USEPA, 2001 and Wathes et al., 1998). The principles used to govern the monitoring of stack emissions from factories are not applicable to these animal production facilities. Even in tunnel ventilated buildings with as few as four exit fans, it is not well defined as to where to put the sensors, whereas it is a rather simple task to determine the location of the sensor(s) in a stack from a factory. Constant, uniform emissions from a factory are quite different than emissions from an animal confinement operation. Gaseous and particulate emissions from these animal facilities are governed by many parameters, some controllable and some not. Within the building, diet, size, season, and feeding activity all affect the concentrations of gases and particulates emitted from that facility (ISU, 2002 and Zhu et al., 1997). The type of manure storage such as depth and covering also impact the emissions (Harper et al., 2000, Sharpe, et al., 2002 and Zahn et al., 2001). The difficulty of taking measurement at the property line or around facilities is compounded by wind direction, wind speed, time of day, time of year, horizontal and vertical distance (Pfeiffer, 2004). Add in the problems associated with instrument variability and ammonia measurements in general, and then the assessment of emissions from confinement facilities becomes a very difficult undertaking (Sumner, A.L., 2004).

Site Descriptions

The two lagoons are located in northern Missouri. The Whitetail Site with the biocover is located just north of Unionville, MO., and the uncovered lagoon at the Locust Ridge Site is located south of Lucerne, MO. The lagoon at Whitetail occupies an area of 14,880 m^2 at a depth of 7.3 m. It serves approximately 8800 pigs and is part of a multicomponent manure management program. The lagoon was covered with a Bio-cap^{TM} geotextile cover manufactured by Amoco and distributed by Baumgartner Environics, Olivia, MN. The lagoon at Locust Ridge occupies an area of 14190 m^2 at a depth of 7.3 m. It serves approximately 8800 pigs and serves as a primary storage lagoon. This is significantly different than the function of the lagoon at White Tail.

The building site consists of 3 buildings housing approximately 2500 pigs and is located in Boone County, Iowa. Manure is collected in deep pits below each of the buildings. The pits are flushed yearly following the corn harvest and applied to fields. The ventilation system is classified as natural with curtains opening and closing as required to regulate the indoor temperatures. Pit fans (6 per building) are run as programmed by the manager of the site.

Methodology for Lagoon Sampling Systems

Three sampling lines for each site were built using a combination of Teflon tubing, foam insulation, aluminum tape and a self-controlling heat tape system. The sampling lines ranged from 50 feet to 300 feet in length and were located such that one sampling line was over the middle of the lagoon, another on the north berm and another on the south berm. The sampling lines were constructed by wrapping aluminum tape around Teflon tubing (PFA, 1/2in ID). The Raychem^R (Menlo, CA) heating system was run along this line. This combination was then wrapped with another layer of aluminum tape. The heating system was set to maintain a temperature of 40° F. The entire line, consisting of the Teflon tubing and heating line wrapped with aluminum tape, was then placed inside 6 foot long tubes of black pipe insulation (5/8" ID x ½"thickness) placed end-to-end. The entire sampling line was then placed into another series of black pipe insulation tubes (2 1/8" ID x ½" thickness). Duck tape was used to seal the seams forming a continuous sampling line. To minimize damage from rodents, snow and soil surface temperatures, the berm lines were suspended above ground using metal posts. The lines extended into the heated trailer where they were attached to the sampling manifold system. The manifold system consisted of a 8-port sampling valve and controller from Valco Instruments (Houston, TX), a Teflon^R manifold, and 2 vacuum pumps. The valve was designed such that while one port is being sampled via the manifold on one vacuum pump, the other seven ports are linked to a common exit port that is attached to the other vacuum pump. The valve is designated SC, for common outlet configuration and MW, for low pressure. The valve was controlled by a high torque multiposition microelectric actuator from Valco linked to a Valco DVSP4 digital valve sequencer that served as a timer to rotate the valve to a different port every 15 minutes. The vacuum pump was set so that each of the seven non-sampling ports and associated sampling lines were pumped at a rate of 3 liters/minute. The continuous pumping served a dual function: 1) to allow for instantaneous measurements when the port is switched to sampling mode since there is no dead volume, and 2) to minimize the affects of NH_3 sticking to the tubing, hence creating a pseudo equilibrium between the air and the tubing. The port being sampled was pumped at a rate set to just exceed the requirements for the analyzers. Each port was held in the sampling mode for 15 minutes. Ports 1, 3, 5, and 8 were connected to the sampling lines from 2 meters above the lagoon, north berm, 1 meter above the lagoon, and south berm. Ports 2, 4, 6, and 7 were connected to lines in the trailer from which the air in the trailer was drawn though activated carbon resulting in a "blank" air. The purpose of the "blank" air was to allow the analyzers to return to baseline between sampling.

Micrometeorology

Floating platforms were constructed using 8" PVC pipe filled with Styrofoam balls and sealed at both ends. Attached to the PVC pipes that served as pontoons was a welded aluminum frame that had a central mast extending greater than 2.0 meters above the above the surface of the lagoon. The entire platform was placed in the center of each lagoon and attached to cable(s) that crossed the lagoon. The cables were anchored at the berms. The platform was free to move up and down depending on the liquid levels in the lagoon. However, there was some flexibility resulting in rotational movement relative to the winds. This resulted in errors relative to the measurement of wind direction. Since wind direction was used only in selecting the proper berm for background concentration corrections, it was not a serious problem. Micrometeorology sensors were attached to the masts at heights equal to 0.25, 0.5, 1.0, and 2.0 meters above the surface of the lagoons. A Model 03001 Wind Sentry (R.M. Young, Grand Rapids, MI) was placed at a height of 2.0 meters to measure wind speed and direction. At the other heights a Model 03101-5 anemometer from R.M Young was installed to measure wind speed only. A CS500 Temperature and Relative Humidity Probe (Campbell Scientific, Logan UT) was placed at a height of 2.0 meters to measure air temperature and relative humidity. Model 107-L Temperature probes from Campbell Scientific were placed at the other heights to measure air temperature only. Data was collected on a Model 21X data logger from Campbell Scientific. A 12 volt system using a MSX20 solar panel from Campbell Scientific was used to power the system. A cell phone system consisting of a COM100 Motorola analog cellular phone package and a

COM210 phone modem from Campbell Scientific were installed for direct communications to Ames, Iowa. Data averaged over 10 minute intervals was downloaded to Ames from the data logger using this system.

Instrumentation for Ammonia Measurements

Ammonia concentrations were determined using a Model 17C Chemiluminescence Analyzer (Thermo Environmental Instruments, Franklin, MA). The Model 17C utilizes the reaction of nitric oxide (NO) with ozone (O_3) as its basic principle of detection. The sample is drawn into the instrument by an external pump and after it reaches the reaction chamber, it mixes with ozone, which is generated by the internal ozonator. The following chemical reaction then occurs $NO + O_3 = NO_2 + O_2 + \text{Light}$. The intensity of the luminescence, which is detected by a photomultiplier tube, is proportional to the concentration of NO in the air being sampled.

To measure the total nitrogen concentration (N_T) both nitric oxide (NO_2) and ammonia (NH_3) must be transformed to NO prior to reaching the reaction chamber. This transformation takes place in a stainless steel converter heated to approximately 775°C. Upon reaching the reaction chamber, the converted molecules along with the original NO molecules react with ozone. The resulting signal represents the N_T reading. In the NO_X mode, the gas passes through a low temperature converter that converts NO_2 into NO without converting any of the ammonia. This gas stream passes into the reaction chamber where the signal generated is the sum of the original NO plus NO_2 and is referred to as the NO_X fraction. The NH_3 concentration is then determined by subtracting the signal obtained in the N_T mode from the signal obtained in the NO_X mode.

Instrumentation for Hydrogen Sulfide Measurements

A Model M101A H_2S Analyzer (Advanced Pollution Instrumentation, San Diego, CA), was used to measure the concentrations of hydrogen sulfide. The M101A is equipped with a low temperature (315°C) converter that converts H_2S to SO_2 while leaving other gases in the sample unaffected. Sample gas is drawn into the analyzer by an external pump and passes through a scrubber to remove all traces of naturally occurring SO_2. The converter then converts the H_2S into SO_2 which is measured by fluorescence. However, a recent report from Battelle (Sumner et al., 2005) indicates that other sulfur-containing compounds are also reduced and subsequently reported as H2S. What is actually being measured, reduced sulfur or H_2S, is likely to receive attention in the near future. The results given in this paper are presented as H_2S.

Instrumentation for Methane Measurements

A Model 55C Analyzer (Thermal Environmental Instruments, Franklin, MA) was used for the detection and quantitation of methane and volatile organic compounds (VOC's). The instrument uses back-flush chromatography with flame ionization detection (FID) to measure methane and VOC's. A proprietary GC column achieves complete separation of methane from all C2 and greater carbon containing compounds and the VOC's. Methane passes through the GC column directly for analysis while all other components are retained on the column. CH_4 is measured by the FID, and then the gas flow is switched to allow purging of the column and the subsequent measurement of all the retained compounds by the FID. The VOC's elute as a large, broad peak and quantitation is accomplished relative to some carbon containing compound such as hexane or propane. Results are reported as propane, hexane, or carbon equivalents.

Instrument Calibration

Instruments were calibrated weekly using cylinder gases (Scott Specialty Gases, Plumsteadville, PA). The highest quality standards are necessary for the primary calibration gases. For ammonia, Scott's Title V^R Grade standards were used. For hydrogen sulfide, EPA Protocol^R Grade standards were used. Methane was an EPA Certified Grade. Lower quality gas standards were used for the weekly calibrations; however, they were verified as to their actual concentrations against the primary standards. The weekly calibrations were done at a single concentration which was chosen based on the actual real-time data such that that the concentration was in the middle of the ranges being measured. For linearity checks the primary calibration standards were diluted using a gas dilution system. Two systems were used during the study. For the first half of the study, a Model 700 (API, San Diego, CA) was used. This system was a standard dilution system with no special coatings and the mass flow controllers were calibrated but not with NIST traceable standards. For the second half of the study a Series 4000 (Environics, Boston, MA) gas dilution system was used. This system was calibrated with NIST traceable standards and all transfer lines and valves were silanized to minimize problems with ammonia and hydrogen sulfide.

Data Retrieval

At the beginning of the project, the sites were visited weekly. Data that was stored internally by each analyzer was downloaded to a PC and brought back to Ames for processing. Problems existed with the TEI equipment because its software was compiled on an older version of Windows^{R} that was not completely compatible with the newer PC's. In January, following programming by Mr. Scoggin at NSTL, Lab View^{R} (National Instruments, Austin, TX) was installed along with internet capabilities at each site. By using Lab View^{R}, the instruments could be monitored and controlled remotely and data could be downloaded from the locations to Ames. This could be done more frequently resulting in a decrease in lost data. For this reason the last 6 months of data collection were far more comprehensive then the first 6 months.

Methodology for Natural Ventilated Buildings

Instrumentation for Ammonia

The system used was an IonPro IMS (Particle Measuring Systems, Boulder, CO); an air cleanup unit, Model 64-01 (Parker-Hannifin Corporation, Tewksbury, MA); and an continuous oil-less air compressor Model 1000-25B (Jun-Air, Buffalo Grove, IL.). The sample is pulled into the analyzer by a small pump and forced over a semi-permeable membrane on the outside of a reaction cell. The membrane allows materials of interest to enter the detection cell, while other materials pass on, thus removing many possible interferents. Purified dry instrument air sweeps the membrane on the inside of the cell and delivers the sample to the reaction region. There the sample is ionized by a weak plasma formed by a small nickel-63 radioactive source. A dopant material is added to the flow to enhance the ionization process and increase specificity. The ionized sample molecules drift through the cell under the influence of an electric field. An electronic shutter grid allows periodic introduction of the ions into a drift tube where they separate based on charge, mass, and shape. Smaller ions move faster than larger ions through the drift tube and arrive first at the detector. The current created at the detector is amplified, measured as a function of time, and a spectrum generated. A microprocessor evaluates the spectrum for the target compound and determines the concentration based on the peak height

The analyzer is equipped with a 4-port valve that allows air to be constantly pumped through the tubing connected to each port, minimizing delay times and carryover. The on-board computer switches to the requested port at selected intervals allowing a small amount of sample to enter the cell. The analyzer is also equipped with a permeation tube, which under fixed temperature, and carrier gas flows, allows a known concentration of ammonia to enter the cell to be used as in internal standard for calibration purposes.

Results and Discussion for Naturally Ventilated Buildings

The location of the analyzer is critical in regards to the concentrations being measured. Distance from the buildings as well as the distance above the buildings impact the resulting concentration measurements. As shown in Figure 1, there is a vertical gradient with regards to ammonia concentrations when measured between buildings in July as well as considerable variations within each height. Placing the analyzer 100 ft downwind of the buildings results in the variations shown in Figure 2. The analyzer was setup to measure ammonia concentrations at heights of 3 feet, 20 feet, and 40 feet. Data in this figure show that not only are there differences in ammonia concentration due to height, but also due to time of day. Concentrations were highest between 4:00 pm and 10:00 pm. The affect of horizontal distances on ammonia concentrations are shown in Figure 3. The sampling points were 6 feet above ground level and increasing distances up to 90 feet (all are downwind). The results as shown in this figure clearly indicate a rapid decline from 1000 ppbv ammonia at a distance of 3 feet to less than 50 ppb at a distance of only 90 feet.

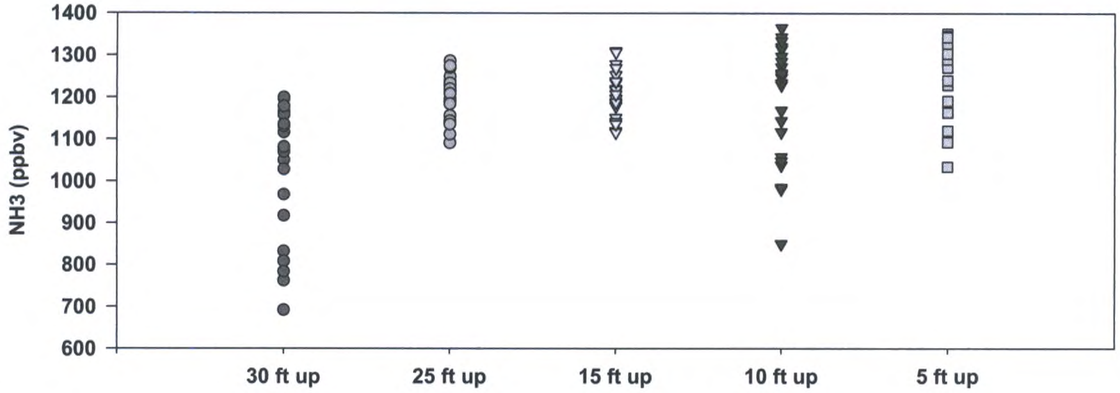

Figure 1. Variability of Ammonia Concentrations Due to Height

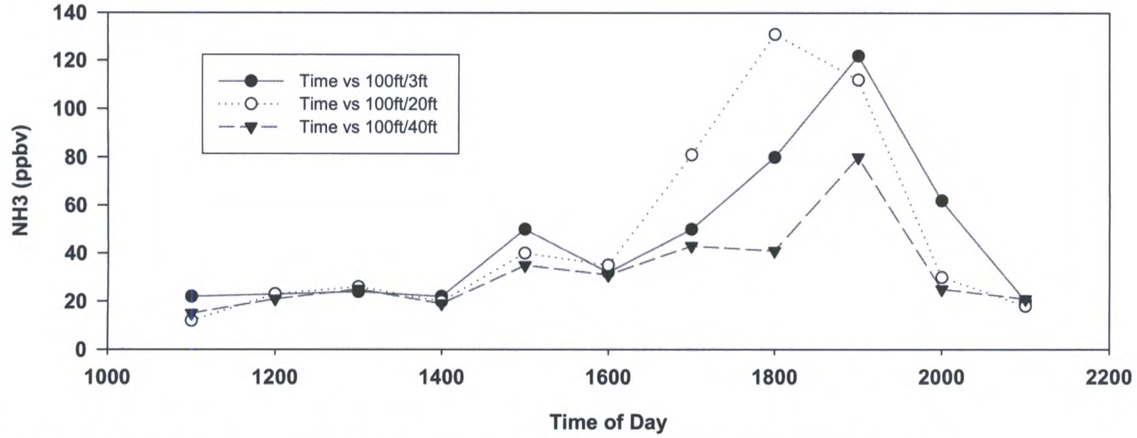

Figure 2. Affect of Height on Ammonia Concentrations 100 Feet Downwind

It is interesting that this rapid decline occurs over such a short distance. Since most property lines are further from the buildings than the 90 feet in this study one must question the validity of using the property line as the measuring point for many proposed and/or enforced regulatory standards. Now that the affects of distances have been examined, what happens when the wind changes direction? An example of the affects of changing wind directions are presented in Figure 4. The differences range from 1000 ppbv ammonia when the analyzer is downwind to less than 20 ppbv ammonia when the wind direction reverses and the analyzer ends up being upwind. Finally, what is the variability of ammonia concentrations if the analyzer is placed directly in front of a pit fan such that the pit fan's exhaust is being monitored directly? This is shown in Figure 5. Presented in this figure are concentrations over a 24 hour period in August, 2005 from an analyzer placed 20 feet from a pit fan that was running continuously at a constant velocity. There was no mechanical mixing of the deep pit contents at this time. This variability may have been due to the biological activity in the deep pit, but more likely was due to changes in animal activity. Are the pigs active and feeding, or are they resting? Disturbing the pigs prior to taking a measurement could lead to elevated ammonia concentrations that may not reflect average emission concentrations from the production facility.

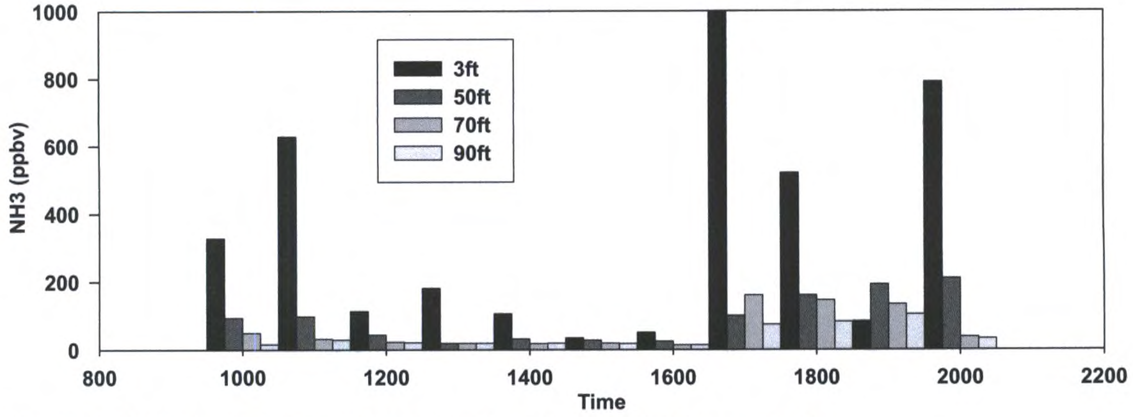

Figure 3. Affect of Distance Downwind on Ammonia Concentrations

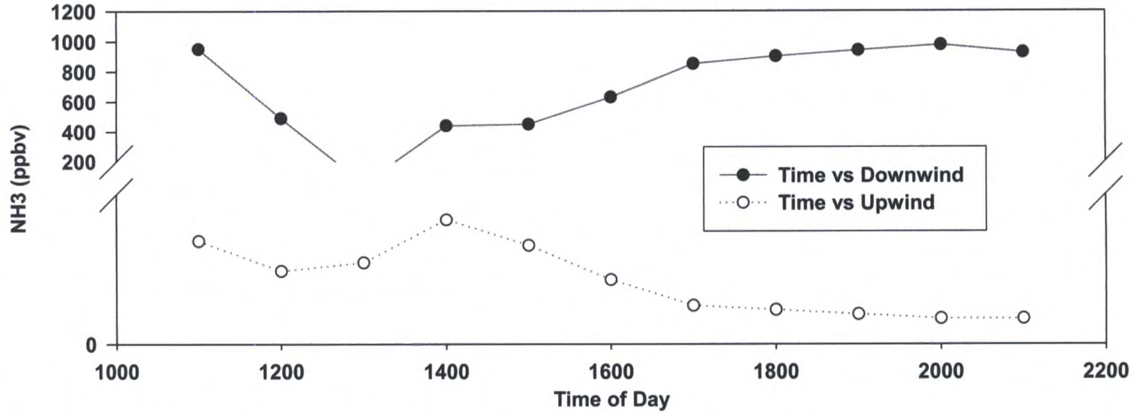

Figure4. Affects of Wind Direction on Ammonia Concentrations

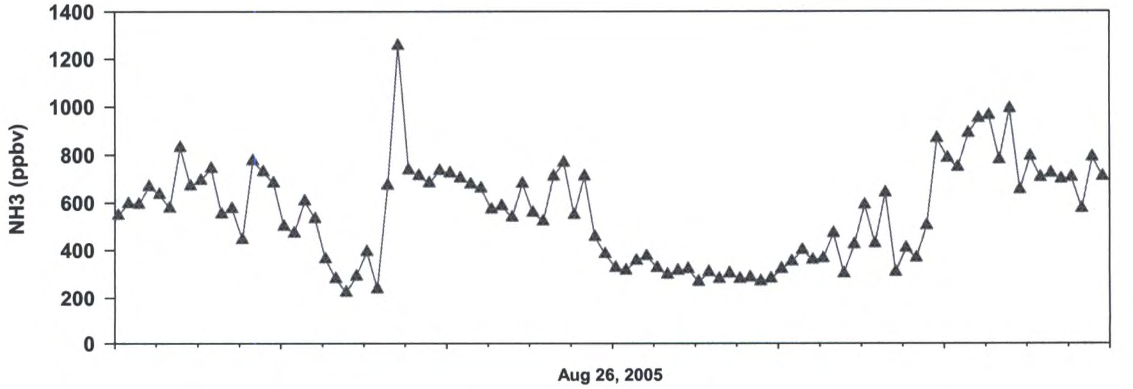

Figure 5. Variability of Ammonia Concentration in Front of a Pit Fan

Results and Discussion for Lagoons

From the previous figures, one can see that choosing a sampling point that yields a representative concentration is a very difficult, if not impossible, task. Measuring concentrations of gases above and on the berms from lagoons presents the same problems. The following discussion is focused on two lagoons, one covered and the other uncovered (open air), with emphasis on daily and seasonal variations as well as sampling height above the lagoon. Wind affects will also be discussed relative to a sampling location on one of the berms. Data for ammonia, hydrogen sulfide and methane are presented.

Figures 6 and 7 show the concentrations of ammonia two meters above the center of a covered and uncovered lagoon, respectively. The ammonia concentrations range from greater than 5000 ppbv to less than 100ppbv, a 50 fold difference. To rely on a single measurement as an indicator of the emissions from any swine production facility can only result in questionable conclusions.. Given this high range of concentrations the importance of long-term continuous monitoring as part of any research and/or regulatory investigation becomes quite evident.

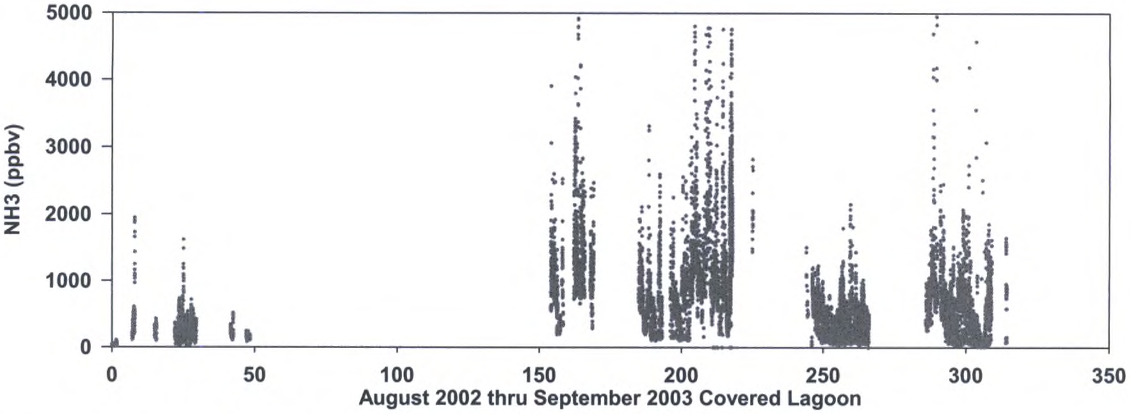

Figure 6. Ammonia Concentrations from a Covered Lagoon

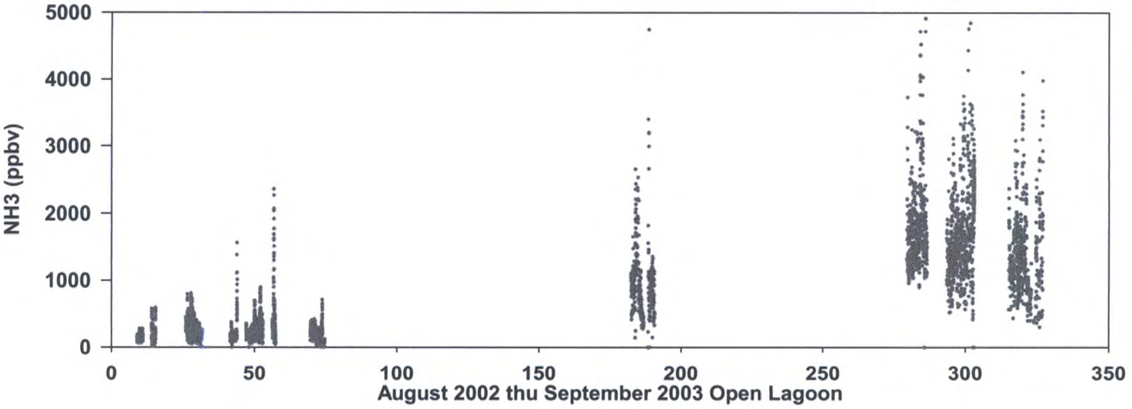

Figure 7. Ammonia Concentrations from Uncovered Lagoon

Due to analyzer problems and power outages the number of data points collected at the two locations were quite different. Also, there were long periods of time in which no data was collected. A direct comparison using all the data points yields averages that are significantly biased by the seasonality of the concentrations and other variables. As shown in Figure 7, the time of year has a major impact on the concentrations of ammonia over the lagoons.

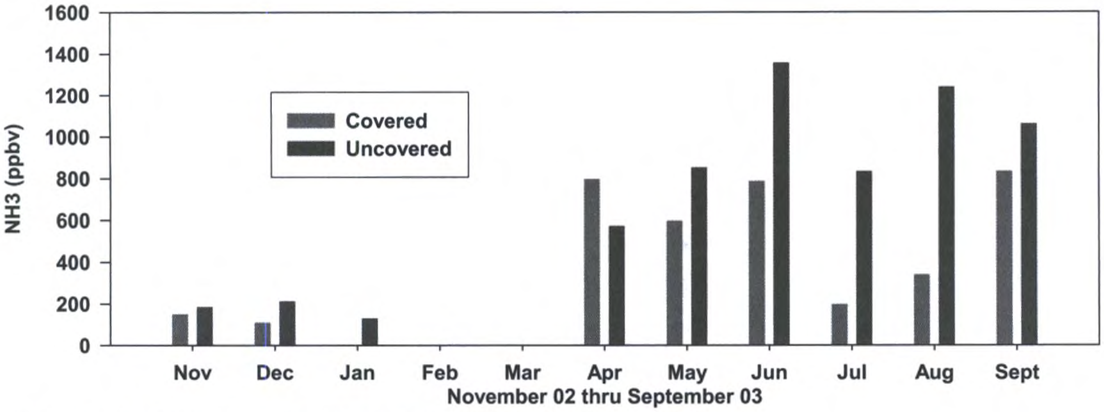

Figure 8. Daily Ammonia Concentration Averages By Month

In this figure, the daily average ammonia concentrations from paired days (as close as possible) averaged over each month are represented. The monthly ammonia concentration averages vary considerably, not only between months of the year, but between the covered and uncovered lagoon. The average ammonia concentrations range from less than 200 ppbv in the winter to more than 1400 ppbv during the summer. Overall, there are significant differences due to the cover with the exception of April. There does not seem to be an explanation for this reversal of concentrations in April. The volume of the liquid in the uncovered lagoon may have been supplemented with clean water as part of the management program resulting in a decrease in ammonia concentration. Concentrations for the covered and uncovered lagoons were 414 ppbv and 805 ppbv, respectively. This represents a 49% difference that is significant at a p-value of <0.01.

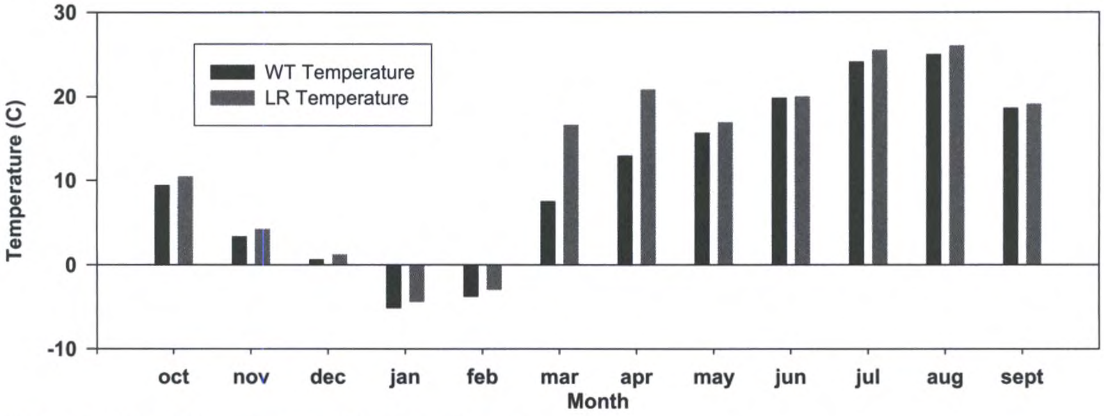

Figure 9. Monthly Average Temperatures

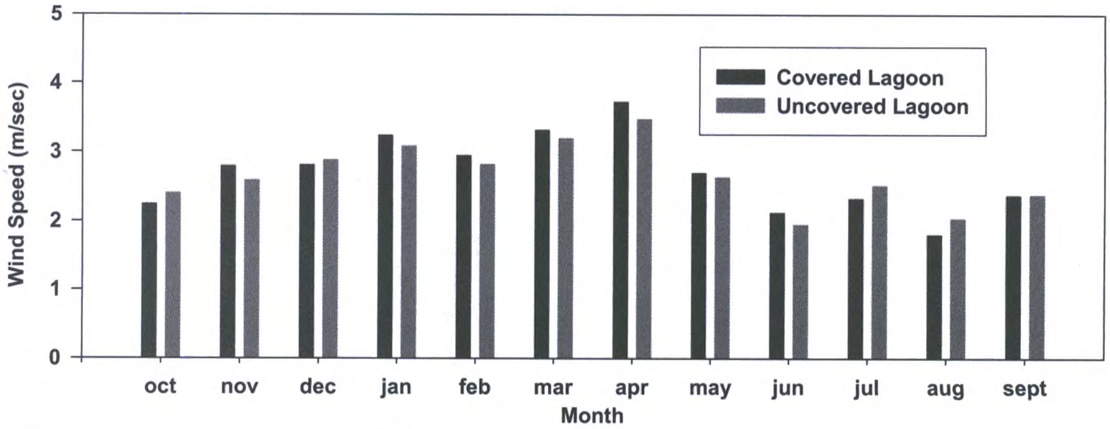

Figure 10. Monthly Average Wind Speeds

The two lagoons were separated by over 30 miles so it is possible that wind and temperature differences played a role in the concentration differences noted in Figure 8. However, based on the data presented in Figures 9 and 10, this is not the case.

From the previous figures, the variations in ammonia concentrations due to season and covering are significant; however, the variations are not limited to long term changes. An example of this is shown in Figure 11. In this figure, ammonia concentrations are shown for a 24 hour period with analysis done every minute. The sampling location is two meters above the center of the uncovered lagoon. The ammonia concentrations varied from 2200 ppbv to over 3000 ppbv during the 24 hour time period. The values peaked early in the morning and again at 1500 hours. Wind speed was rather constant at 2.6 m/s, but the wind direction changed from 50 degrees to 130 degrees during the day. Data concerning the transferring of waste into the lagoon was not generated and this could be a key factor. Another factor that affects concentration values is the height of the sampler above the lagoon. For this study, two sampling lines were located above the center of the lagoon. One was 1 meter above the lagoon, and the other was 2 meters above the lagoon. Figure 12 shows the concentration data from these two locations. Note that the real sampling times are actually offset approximately 1 hour due the sampling schedule that included blanks and berm sampling over a 2 hour cyle that was discussed previously.

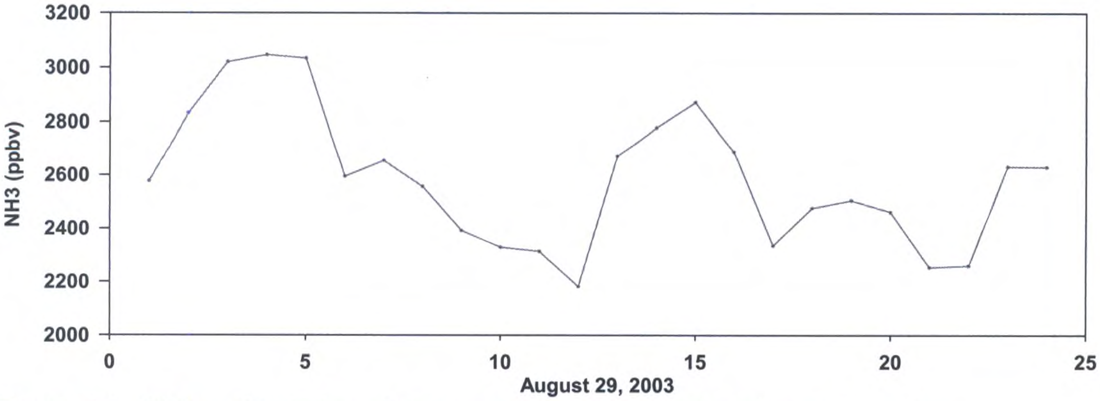

Figure 11. 24 Hour Variation of Ammonia Over the Center of Open Lagoon

The data presented in Figure 12 indicates that the concentrations at 1 meter can actually be less than the concentrations at 2 meters. Several factors such as low wind speed, affects of the berm, wind direction and relative humidity could be used to explain this occurrence. The actual design of the sampling tower and attachment of the two sampling lines could also account for this fact.

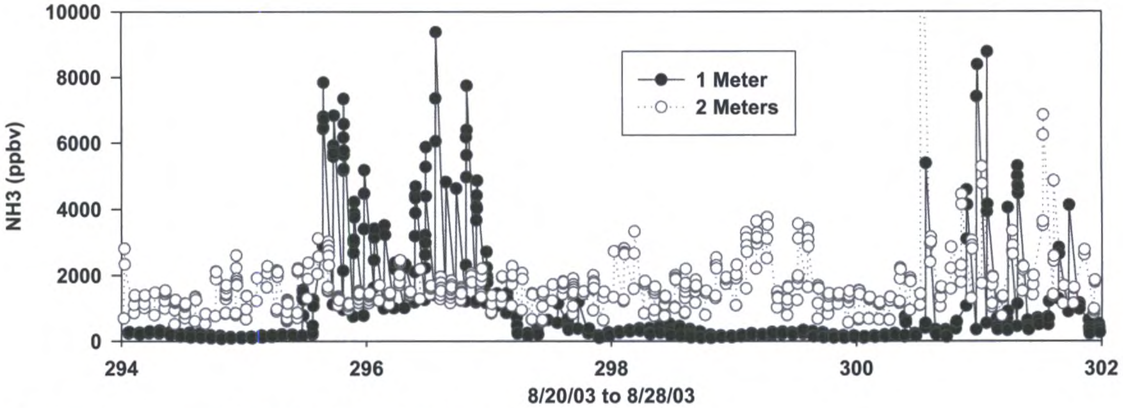

Figure 12. 1 Meter Verses 2 Meters Sampling Height

The affect of wind direction concentrations of ammonia can be observed by looking at a plot of the south berm concentrations verses wind speed using a wind rose diagram. This is shown in Figure 13. Due to the construction and mounting of the floatation platform the wind directions are actually 80 degrees larger than those shown in the figure. For example a wind direction of 20 degrees is actually 100 degrees and a wind direction of 300 degrees is actually 20 degrees. Winds from the north cross over the lagoon before reaching the south berm and thus the concentrations of ammonia are higher. Winds coming from the south pass over open land before reaching the berm and thus reflect the lower background concentrations of ammonia. Three dimensional wind data were not taken during the study. Dissecting the wind direction into vertical and horizontal components might lead to some interesting conclusions regarding the transport of ammonia from the production facilities into the atmosphere.

The same variability that exists for ammonia also exists for hydrogen sulfide. The average paired daily concentrations of hydrogen sulfide were 8.8 ppbv and 25.0 ppbv for the covered and uncovered lagoon, respectively. This represents a 64% reduction in hydrogen sulfide concentrations that is significant at a p-value of <0.01. The hydrogen sulfide concentrations for the uncovered and covered lagoon are shown in Figures 14 and 15, respectively.

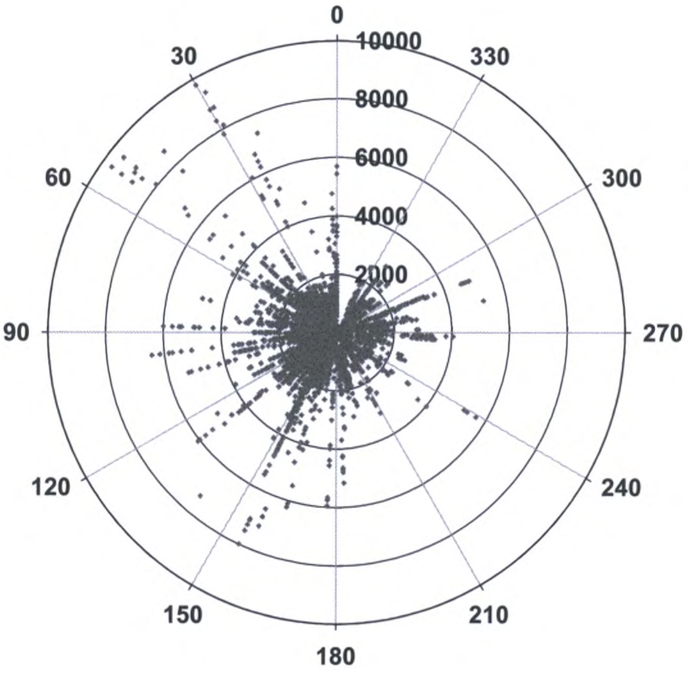

Figure 13. Ammonia Concentration Verses Wind Direction

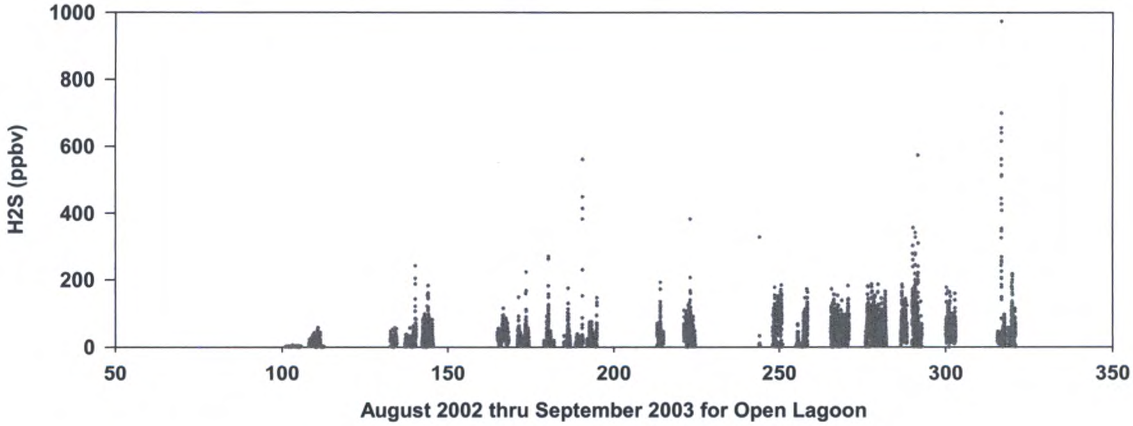

Figure 14. Hydrogen Sulfide Concentrations from Uncovered Lagoon

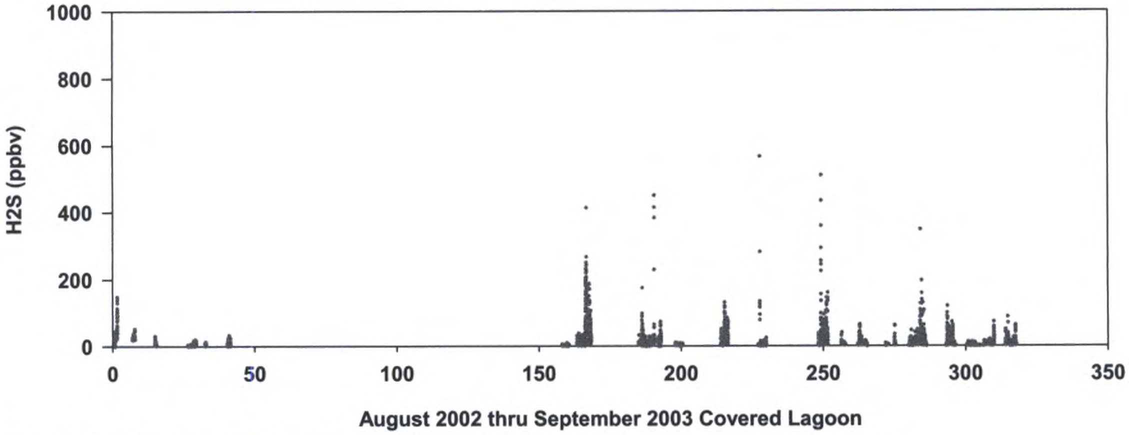

Figure 15. Hydrogen Sulfide Concentrations Above a Covered Lagoon

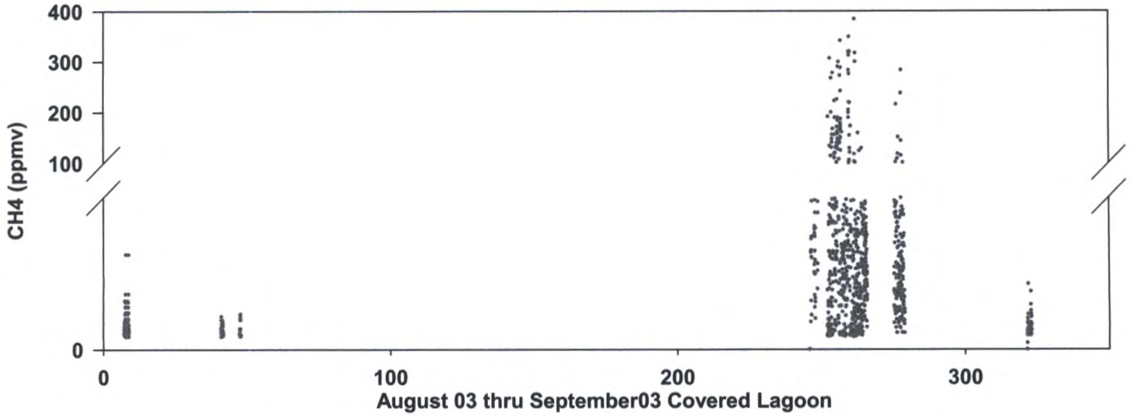

Figure 16. Methane Concentrations Above a Covered Lagoon

The variations in methane concentrations shown in Figures 16 and 17 were similar to those from ammonia and hydrogen sulfide with one exception. The methane concentrations were higher above the covered lagoon, than the open lagoon. This is possibly due to the increased conversion of the volatile organic compounds to methane as a result of the trapping effect of the cover and/or increased anaerobic conditions. Large bubbles that formed under the cover demonstrated the semi permeable nature of the cover. The paired daily average concentrations for methane were 13.2 ppbv and 24.1 ppbv for the uncovered and covered lagoons, respectively. This 49% increase was significant at a p-value <0.01.

The instrument used for the measurements was the TEI Model 55C Methane/Non-Methane Hydrocarbon Analyzer. Known concentrations of methane were presented to the instrument via the manifold system and a diluter connected to a 100 ppmv cylinder of methane. The results clearly indicated that the instrument was able to accurately measure methane concentrations. However, testing of the non-methane measurement features yielded disturbing results. When propane was presented to the instrument via the diluter and a 100ppm cylinder of propane the results were excellent. Propane is a typical hydrocarbon and these results were not surprising.

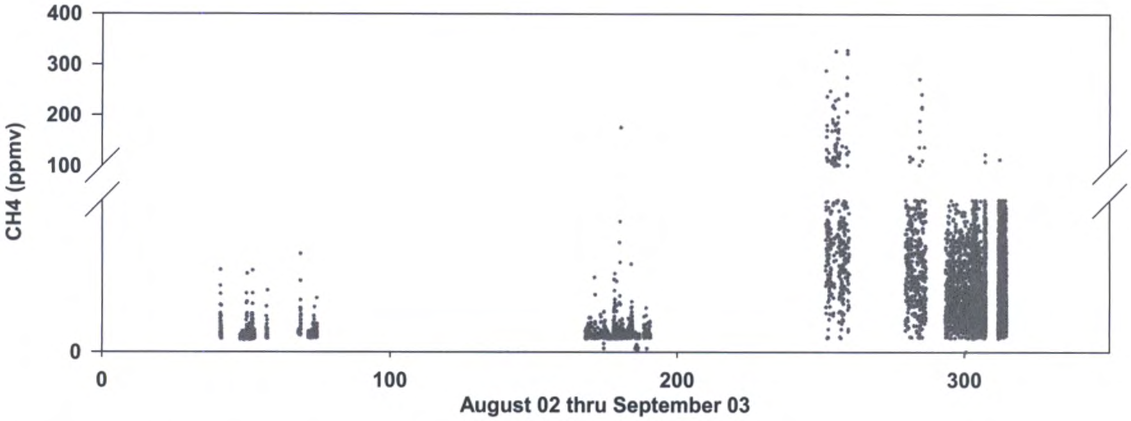

Figure 17. Methane Concentrations Above an Uncovered Lagoon

However, using this instrument for the measurement of other organic compounds associated with lagoon emissions such as acetic acid, butyric acid, propionic acid, and p-cresol may not yield satisfactory results. No response was seen when placing these compounds at high ppmv concentrations directly in front of the inlet for the Model 55C. No peaks were detected, but a steady rise in the background signal was observed. These compounds are not classified strictly as hydrocarbons because of the presence of other side groups such as COOH (acids), OH (phenol), and SH (mercaptan). These compounds are more polar than the traditional hydrocarbons and are likely to adsorb to the column packing material and not elute in a sharp band during the flow reversal process. Acids, aldehydes, ketones, etc., are important constituents of the volatile organics associated with emissions from lagoons, and it is incorrect to assume that the Model 55C will measure them. Even with its limitations, the Model 55C worked well for measuring methane concentrations.

Summary

The measurement of gases from swine confinement operations is not an easy task. Any attempts to apply the methodology associated with the measurement of gases emitted via a smoke stack will result in failure due to the large number of variables associated with the confinement operation. The variability of measured ammonia, hydrogen sulfide, and methane concentrations that have been described in this paper are due to time of day, time of year, distance, and type of storage. Other variables such as diet, animal activity, building type, and ventilation system are currently under investigation by this author and many others. The determination of emission factors and ultimately the pounds of gases emitted from animal confinements on a per day or per year basis will require the concentration data discussed in this paper in order to reach a scientifically sound conclusion.

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Denitrification and Nitrous Oxide Fluxes from Frozen, Manure-Amended Soil

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Abstract

Intensive studies of nitrous oxide (N_2O) fluxes indicate highly variable but significant responses to synthetic fertilizers, composts, and fresh animal manures. Effects of fertilizers on N_2O emissions often vary with fertilizer form, soil characteristics, timing, and rate of application. In the upper Midwest, manures are often applied in autumn with the assumption that denitrification is negligible over-winter when soils are frozen. Little data, however, supports this assumption. Soils collected from crops fields in production were assayed to determine effects of dehydrated manure application on N_2O emissions in winter. Intact cores were incubated 17 days later at field temperature (-2 °C) in the laboratory and N_2O flux and denitrification measured. Nitrous oxide emissions and denitrification occurred in both fertilized and unfertilized soil. Autumn application of dehydrated manure stimulated biological denitrification, compared with un-amended soil, even at -2 °C.

Introduction

Organic agriculture currently represents ½ million hectares of U.S. cropland and interest in conversion from synthetic to organic-based fertilizer amendments is expected to rise with the cost of fossil-fuel-based fertilizers. Agricultural fertilization worldwide contributes more anthropogenic nitrous oxide (N_2O) to the atmosphere than any other single known source [*Bouwmann*, 1990]. Nitrous oxide is photochemically and radiatively reactive and is 296 times more effective per molecule than CO_2 as a greenhouse gas. A greater understanding of factors controlling N_2O flux to the atmosphere for production agriculture soils in the field is needed. Data are lacking that quantify how organic fertilizer products contribute to N_2O emissions in an agricultural production environment and under freezing field conditions.

Agricultural fertilization influence N_2O fluxes, but the response varies with soil properties, fertilizer type, application timing, and rate [*Breitenbeck*, 1986]. Intensive laboratory studies indicate significant response in N_2O flux when soils are amended with synthetic fertilizers, composts, and fresh animal manures. Rarely, however, are fertilization effects tested in a production agriculture environment, especially in the Red River Valley (RRV) ecoregion, where soils tend to remain frozen for five months of the year. Consequently, amounts of N_2O and N_2 produced from denitrification in crop fields at sub-zero temperatures are largely unknown. We aimed to determine if organic fertilizer application would influence N_2O flux and denitrification in frozen soils for crop fields in the RRV. We address this question on working farms for the purpose of addressing the need for data representative of production-oriented agriculture.

Methods

The RRV region, located in the upper Midwestern U.S., is one of the most productive agricultural regions in the world. Soils are lacustrine remnants of the south-easternmost extent of glacial Lake Agassiz, and climate is characterized by long, cold winters (~5 months) and mild to warm, abbreviated summers. In general, RRV soils remain frozen the entire winter, compared to other regions of the Midwest, where freeze-thaw cycles are common. Since soils remain frozen during winter, organic soil amendments are typically applied to crop fields in late-autumn just prior to freeze-up. Conventional, synthetic fertilizers, such as urea, are applied more often in the spring just prior to planting.

To address the question of how manure might alter nitrous oxide flux during winter after autumn fertilization, two 80-acre, homogenously managed fields were selected: one managed conventionally for >50 yrs and one managed organically for >5 yrs. Both soils share similar soil properties, climate, and crop rotations and are located <1 km from each other in Clay County, Minnesota. Between field treatments an uncultivated control site with no history of fertilization was identified. Both were last planted with soybeans and were last fertilized 1.5 yr and 2 yr prior to this experiment, respectively, for conventional and organic fields. On November 20, 2004, the organic field was amended with 67.5 kg N ha^{-1} of a pelletized, dehydrated manure product (Creekwood Farms, Lake Mills, WI) and homogenized into the top 5 cm of soil. Soil temperatures below freezing were recorded one week following manure application and soil cores (0-15 cm depth) collected ten days after soil freezing. Five intact cores were extracted by hand using a 5-cm diameter hammer auger at random points within 8-ha field plots from both conventional and organic fields and immediately placed in cold storage (8 °C). A core from the uncultivated site was also collected. Cores remained below freezing for the duration of the experiment. Soil temperature (0-15 cm) was -2 °C at the time of core collection.

We utilized a laboratory-grade, temperature-controlled freezer (Scientemp Corp.) for the purpose of simulating field temperatures in the laboratory. The day after field sampling, intact cores were extracted from collection tubes and each was carefully placed inside a 1-L glass Mason jar equipped with a septum for gas sampling and allowed to equilibrate at -2 °C for four hours. Included were two empty jars, or blanks, which were treated as samples throughout the experiment. Prior to sampling, covers were removed to introduce fresh atmosphere into the headspace while remaining in the freezer. Jars were capped, and a 15-ml headspace sample was drawn and replaced with an equal volume of N_2 to maintain constant pressure. The headspace was sampled every 0.25 hr to complete a 1-hr time course. Aliquots were immediately injected into 15-ml exetainers (Labco Unlimited) and analyzed for N_2O using a Varian Model 3800 Gas Chromatograph and Combi-Pal auto-sampler. In this system, sample is auto-injected into a 1-mL sample loop, then loaded onto columns and routed through ^{63}Ni electron-capture detector (ultra-pure 95% Argon/ 5% CH_4 carrier gas) detector. Following the incubations, bulk density and percent water filled pore space (WFPS) were determined for each core. The mass of N_2O-N produced was calculated based on a linear time course, following correction for headspace dilution with N_2.

Results and Discussion

Average ($\pm$ standard deviation) N_2O emission for manure-amended soil at -2° C on a mass basis (dw=dry weight) was 0.68 ng g $dw^{-1}hr^{-1}$ N_2O-N ($\pm$0.67), while average emission for soil that was not recently amended was 0.23 ng g $dw^{-1}hr^{-1}$ N_2O-N ($\pm$0.18). Nitrous oxide emission for soil that was uncultivated with no history of fertilization was 0.10 ng g dw^{-1} hr^{-1} N_2O-N. On an area basis (assuming N_2O measured from 0 to 15 cm is emitted at the surface), manure-amended soil emitted 114.40 µg m^{-2} hr^{-1}, compared to 37.65 µg m^{-2} hr^{-1} for un-amended soil.

Denitrification was measured on the same soil cores the following day also at -2° C using the acetylene inhibition technique [*Paul and Beauchamp*, 1989], and denitrified N (N_2O+N_2) measured following the protocol described above. Total denitrification (N_2O+N_2) on a mass basis for manure-amended soil was 1.03 ng g $dw^{-1}hr^{-1}$ ($\pm$ 0.75), while average denitrification for soil that was not recently amended was 0.27 ng g dw^{-1} hr^{-1} ($\pm$ 0.23). There was no evidence of denitrification in the uncultivated soil core. On an area basis, manure-amended soil emitted 173.01 µg m^{-2} hr^{-1}, compared to 43.67 µg m^{-2} hr^{-1} for un-amended soil. Water-filled pore space was similar for both organic and conventional field soils, with average WFPS of 41.4 ($\pm$ 5.0) and 39.1 ($\pm$ 5.8), respectively.

Results indicate biological denitrification at temperatures below freezing for both treatments. Moreover, denitrification was greater for manure-amended soil, compared with soil that was not recently fertilized. These rates were determined 17 days after manure application. If they are representative of winter denitrified-N losses and if these were consistent over the 5 months of winter, then 6.23 kg N ha^{-1} of the added N (9% of the total N input) would be denitrified from frozen, manure-amended soil. Conversely, frozen soil that was not recently amended, either organically or synthetically, would denitrify 1.57 kg N ha^{-1} over-winter. These data suggest denitrification rates increase following application of dehydrated manure in late-fall and point to the importance of microbial activity in frozen soils [*Rover*, 1998]. Moreover, the data suggest that denitrification measurements are essential for understanding the fate of manure N applied to agricultural soils [*Calderon, et al.*, 2005].

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Ammonia Flux and Dry Deposition Velocity Estimated from an Intensively Managed Animal Agricultural Facility in North Carolina

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Introduction

Recent studies in Europe and the United States have reported increasing atmospheric concentration levels of ammonia (NH_3) and ammonium (NH_4^+), especially in regions of concentrated animal feeding operations (Aneja et al., 1998). These higher concentration levels have shown to be directly related to the rapid growth of intensively managed agriculture. At present, ammonia emission and subsequent wet and dry deposition are a significant waste management problem facing animal husbandry and agriculture. In NC, estimates reveal that the swine population contributes approximately 46% of the NH_3-N emissions. This estimate shows a direct link to the recent growth of the swine population in NC. NC is ranked second in the nation for swine production with approximately 10 million hogs in about 2500 hog farms located in eastern North Carolina (Aneja et al., 2000). Areas of scattered local sources (small, rural family farm operations) contribute a wide range of NH_3 emission and dry deposition. Likewise, many environmental problems result from atmospheric ammonia deposition, e.g., particulate matter formation, aquatic and terrestrial eutrophication, and odor emanation.

An experimental study was conducted on the emission and dry deposition fluxes of ammonia under different meteorological conditions, using a micrometeorological technique (micrometeorological gradient and modified Bowen-ratio methods in conjunction with the Monin-Obukhov similarity theory) over natural surfaces in North Carolina where intensively managed agriculture/animal farms are located. Diurnal and seasonal variations of ammonia flux and dry deposition velocity were investigated under a wind range of wind and atmospheric stability conditions yielding hourly variation of NH3 flux and deposition velocity.

The primary objectives of this research are: (1) to measure vertical fluxes of ammonia and related dry deposition velocities from near-surface concentration gradient measurements over natural surfaces in eastern North Carolina downwind of a source; (2) investigate and evaluate the variability of ammonia flux and related dry deposition velocity on a specified natural surface (i.e. grass) with respect to the time of the day, season, and meteorological factors; (3) obtain empirical relations for dry deposition velocity of ammonia; and (4) quantify the fate of atmospherically deposited nitrogen during summer season in North Carolina terrestrial ecosystems (water and land). This particular area of emphasis is chosen because of the obvious lack of data and the expressed need for a better understanding of ammonia flux and dry deposition velocity in eastern North Carolina, where ammonia sources have increased very rapidly in recent years (DAQ, 1997).

Methods and Materials

A series of seasonal field experiments of ammonia concentrations were conducted at the North Carolina State University Air Quality Educational Unit (USDA-ARS, Raleigh, NC) during Fall 2001, Winter, Spring and Summer 2002. This site is a relatively flat, uniform and smooth site with grass or short vegetation, which is located near a small swine production facility. Two chemiluminescent analyzers, TEI Model 17C (TEI, 2004), were utilized in conjunction with a solenoid for each analyzer to alternate measurements between two elevations (2m and 6m). Hourly-averaged measurements of wind speed, wind direction and temperature were also measured at the same two heights (2m and 6m) using a 7m walk-up tower in the horizontally-homogeneous atmospheric surface layer. The general gradient method is used for estimating the vertical flux and the deposition velocity of ammonia (Businger, 1986; Hicks, 1986) (see Phillips et al., 2002; Phillips et al., 2004)).

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Results

Seasonal NH_3 Concentrations: Comparison with Meteorological Conditions

The seasonal NH_3 concentrations reveal that the largest NH_3 concentrations were during the fall measurement campaign, while the highest maximum NH_3 concentration was observed in summer at 2m (41.71 μg m^{-3}). The larger fall average concentrations are due to the lagoon irrigation practices used and relatively warm temperatures (25.11 ± 3.09 °C), whereas, lagoon irrigation was not applied during the other seasonal measurement campaigns. Based on the animal waste management plan used by the Dairy Educational Unit at the measurement filed site, lagoon liquid irrigation was applied to a field southeast of the air quality tower where a small grain overseed (wheat) was cultivated. A relatively small difference of 1.0-0.65 μg m^{-3} exists between spring and summer average NH_3 concentrations during day and nighttime at the two heights (2m and 6m). The winter season had the lowest overall concentrations collected during each seasonal campaign with averages of 1.73 ± 2.00 μg m^{-3} at 2m during daytime; and 1.37 ± 1.50 μg m^{-3} during nighttime.

During this measurement period frequent changes in the sign of NH_3 concentrations gradient and, hence, flux in the afternoon and night were observed, which are the result of the impact of multiple meteorological variables: temperature variation, wind speed variation from 0.90 to 5.0 m s^{-1}, wind direction variation from north to northeast, to east, and to southeast, and relative humidity variation between 98 to 70%. Likewise, a diurnal relationship between temperature and NH_3 concentrations became apparent reflecting typical near-surface diurnal inversion patterns in which as temperature increases (decreases), NH_3 concentrations also increases (decreases). During the fall measurement period, not only were the northeast and southeast wind directions dominant during daytime but also, higher concentrations of NH_3 occurred in the eastern wind sector due to the transport of NH_3 from a swine lagoon located east of the air quality tower. The correlation between greater frequencies of NH_3 concentrations with winds southwest and west of the tower were observed during the winter, spring, and summer suggesting the effects of environmental conditions (grazed fields as a result of dairy cows located south and southwest of the measurement site), while west wind directions show the effects of horse and chicken farms west of the tower.

Seasonal NH_3 Deposition Fluxes

Seasonal averages and ranges of negative deposition fluxes calculated by the gradient method are presented, which occurred when hourly concentration gradients $\left(\partial \bar{c} / \partial z\right)$ were positive and detectable (Phillips et al., 2004). Since, the level detection limit (LDL) defined by the TEI Model 17C manual is 1 ppb (~0.7 μg m^{-3}); measurements collected and gradients calculated using ammonia concentrations below this LDL value have been excluded from estimated NH_3 seasonal fluxes and deposition velocities. Table 1 presents the statistical analysis (average and standard deviation) of seasonal NH_3 deposition fluxes (after limiting criteria based on v_{max} was applied to estimates of deposition velocities, see Phillips et al., 2004) based on hourly-averaged fluxes, where N equals the number of sampling days and n equals the number of sampling hours, and negative flux implies downward flux or deposition. The direction and magnitude of flux change hourly, diurnally and seasonally, suggesting the effect of environmental, meteorological, and stability conditions, as well as irrigation applications (e.g. Fall Season). Nevertheless, consistently throughout each season, deposition mostly occurred during the late afternoon, evening, and the early morning hours. The results of the seasonal statistical analysis show smallest average negative fluxes in Winter 2002, with hourly-averaged deposition fluxes ranging from -0.14 to ~0 μg-NH_3 m^{-2} s^{-1} and an overall average of -0.02 ± 0.03 μg-NH_3 m^{-2} s^{-1}. Spring and summer season-averaged deposition fluxes are about the same (-0.11 ± 0.15 μg-NH_3 m^{-2} s^{-1}), while the average of hourly fall fluxes of NH_3 is -0.14 ± 0.19 μg-NH_3 m^{-2} s^{-1}. The minimum (maximum deposition) fluxes in these seasons ranged from -1.16 to -0.90 μg-NH_3 m^{-2} s^{-1}.

Table 1. Average seasonal NH_3 deposition fluxes and estimated deposition velocity where N=number of sampling days; n=number of measurements].

	NH_3 Deposition Fluxes* (μg-NH_3 m^{-2} s^{-1})	NH_3 Deposition Velocity (cm s^{-1})	
Season	***Daily***	***Day***	***Night***
Summer	-0.11 (±0.14) N=23, n=135	3.94 (±2.79) N=16, n=85	0.76 (± 1.69) N=18, n=50
Spring	-0.11 (±0.15) N=21, n=88	2.85 (±2.01) N=11, n=37	0.62 (±1.04) N=15, n=51
Fall	-0.14 (±0.19) N=11, n=57	2.82 (±1.98) N=8, n=34	0.07 (±0.17) N=10, n=23
Winter	-0.02 (±0.03) N=15, n=71	2.41 (±1.92) N=9, n=30	0.19 (±0.27) N=12, n=41

* Negative flux is depositing downwards.

Seasonal Ammonia Deposition Velocities

Estimating only the aerodynamic resistance, r_a, the maximum possible deposition velocity ($v_{max} = r_a^{-1}$) has been used to validate estimated deposition velocities with measured meteorological conditions, where $-v_{max}$ is the maximum possible emission rate (Wyers and Erisman, 1998). However, this is based on the questionable assumption that the resistance for the transfer of ammonia is identical to that of momentum. Therefore, we applied a relaxed criterion as an alternative to the assumption of $v_d < v_{max}$, where we consider from the bulk transfer method and considerable experimental evidence (Arya, 1977; 2001), of heat and mass being transferred more efficiently than momentum under unstable and convective conditions. Our relaxed criterion for acceptable values of v_d is that $v_d \leq 2\ v_{max}$ under unstable and convective conditions and $v_d \leq v_{max}$ under stable conditions. Seasonal assessments of v_{max} for all hourly samples of deposition flux show seasonal variations in the v_{max} values due to seasonal influences on wind speed and stability.

Estimates of v_d that did not meet the above relaxed criterion were considered to have large uncertainty in the estimated v_d, and excluded from any further analysis. Seasonal averages shown in Table 2 represent an average of all hourly NH_3 deposition velocities over the number of observation days and are further divided into average daytime and nighttime deposition velocities. They meet our relaxed criterion based on v_{max} and are considered to be more reliable than those excluded.

Summer measurements yielded the largest average daytime deposition velocity of 3.94 ± 2.79 cm s^{-1} while winter season gave the lowest $v_d = 2.41 \pm 1.92$ cm s^{-1}. The average values for daytime v_d during spring and fall seasons are about the same (2.8 ± 2.0 cm s^{-1}). Conversely, nighttime estimates of v_d are much smaller, especially during fall (0.07 ± 0.17 cm s^{-1}) and winter (0.19 ± 0.27 cm s^{-1}) seasons. These daytime and nighttime differences are largely due to different stability conditions. The highest average deposition velocities were generally observed during unstable and near-neutral conditions and lowest values during very stable conditions (Table 2).

Table 2. Average seasonal Stability Classification for estimated deposition velocity [where N=number of sampling days; n=number of measurements].

	Stability Classification for Deposition (cm s^{-1})			
	Summer	*Spring*	*Fall*	*Winter*
Unstable (Ri<0)	4.42 (±2.65) N=12, n=72	3.03 (±1.66) N=6, n=23	3.58 (±1.59) N=5, n=26	3.00 (±1.87) N=8, n=22
Moderately Stable (0≤Ri<0.14)	2.37 (±2.32) N=12, n=22	2.14 (±1.95) N=9, n=30	0.88 (±0.60) N=3, n=4	0.50 (±0.54) N=12, n=24
Very Stable (Ri≥0.14)	0.07 (±0.11) N=17, n=41	0.09 (±0.10) N=13, n=35	0.03 (±0.03) N=10, n=27	0.07 (±0.09) N=10, n=25

Turbulence and Stability Effects

Micrometeorological variables including wind speed at 10m or friction velocity, atmospheric stability, surface heat flux and moisture flux affect turbulence transfer through the surface layer. Friction velocity, a measure of mean wind shear and shear-generated turbulence near the surface in both the canopy layer and above the canopy homogeneous surface layer, is noted to be well correlated with dry deposition velocity and one of the most important variables (Arya, 1999). A regression analysis reveals that a strong relationship exists between friction velocity and estimated deposition velocities. The results of this procedure are based on the combination of seasonal data stratified with respect to stability (unstable, moderately stable and very stable categories) with corresponding regression equation and R^2 values. All seasons display strong correlations with R^2 values of 0.74, 0.54, and 0.86 based on power regression curves for unstable, moderately stable, and very stable conditions, respectively.

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Abating Ammonia Emission from Dairy Barns Through Feed, Herd and Bedding Management

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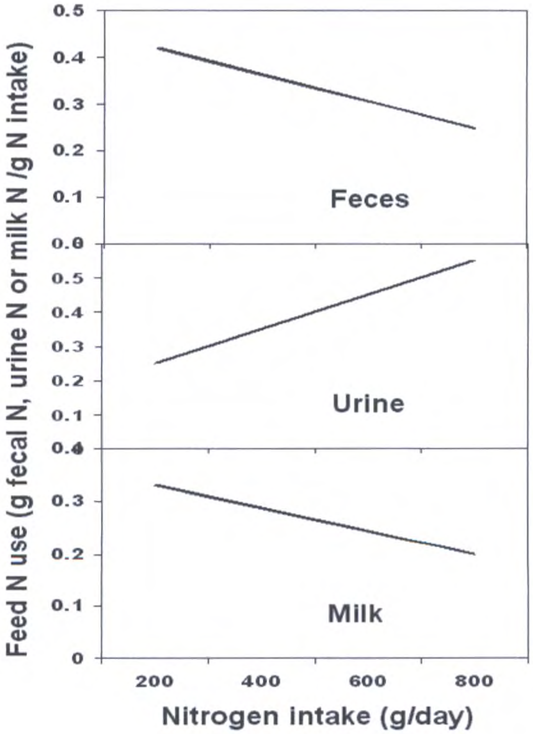
Dairy farms are thought to emit large amounts of ammonia and therefore contribute to nitrogen (N) fertilization of natural ecosystems and provide precursors for particulates that adversely affect visibility and human health. The 2003 NRC report "Air Emissions from Animal Agriculture" (NRC, 2003) made an urgent call for process-based research that assists producers and regulatory agencies in developing strategies that improve air quality. Only about one-fourth of the crude protein (N) fed to a dairy cow is converted into milk, the remainder is excreted in manure. About one-half of the nitrogen in manure is excreted in urine, which can be converted quickly to ammonia and lost as gas. Ammonia production and loss can occur rapidly in the barn and continue through manure storage and land application. Some losses of N as ammonia gas are inevitable, but ammonia N loss can be reduced, and the fertilizer N value of manure can be maintained, through good management.

Figure. 1. General relationships between N fed to dairy cows and N in milk, feces and urine (adapted from Castillo et al., 2000)



Only approximately 20 to 35% of the N (crude protein) fed to dairy cows is converted into milk (Fig.1). When recommended protein levels are fed to dairy cows, manure N is excreted approximately equally in urine and feces. Feeding N to dairy cows in excess of their requirements dramatically increases urine N excretions. About three-fourths of the N in urine is in the form of urea. Urease enzymes, which are present in feces and soil, rapidly convert urea to ammonium. Ammonium can be transformed quickly into ammonia gas. Feces contain little or no urea. For this reason urinary N is much more vulnerable to ammonia volatilization than is fecal N.

Some Approaches to Reduce Ammonia Losses from Dairy Barns

Put More Feed N into Milk, Not Manure

One of the most reliable approaches to reducing ammonia emissions per unit of milk produced is to increase level of milk production per cow. On Wisconsin dairy farms, the efficiency by which the crude protein (CP) contained in feed is converted into milk (i.e., feed N use efficiency) varies according to production practices. Milk production and feed N use efficiency are highest on farms that use total mixed rations (TMR), that balance rations four times per year, and milk thrice daily (Table 1). These practices put more feed nutrients into product (milk), and less into manure.

Table 1. Impact of feed management and milking frequency on milk production, and feed N use efficiencies (FNUE) on 54 Wisconsin dairy farms (Powell et al., 2006)

Practice	Practice use	Milk Production	FNUE
		lbs/cow/d	%
Use TMR	Yes	74a[†]	27a[†]
	No	57b	24b
Balance rations 4 times/year	Yes	67a	26a
	No	54b	21b
Milk thrice daily	Yes	88a	33a
	No	63b	25b
Use Posilac®	Yes	82a	29a
	No	61b	25b

[†] within a practice, means followed by different letters differ significantly ($P<0.05$).

Over the long term, continued genetic selection of cows for high milk production potential will be a very effective means of reducing ammonia N emissions per unit of milk produced. Furthermore, increasing production per animal would decrease the number of cows needed to meet the market demand for milk.

Feed the Correct Amount and Type of Crude Protein to Dairy Cows

Diet formulation to eliminate excess CP usually reduces feed cost, and it is one of the most effective tools for reducing emission into the atmosphere of N containing compounds from dairy farms. Nitrogen excretion by dairy cows via urine, and therefore the amount of manure N susceptible to ammonia loss, is highly influenced by the amount and type of protein fed. As the amount of protein in feed exceeds what is required, relatively less N goes into milk and more goes directly into urine (Fig. 1).

Significant reductions in urine production can be obtained by reducing dietary protein levels. For example, if 17.5% dietary protein currently represents an industry average for lactating cows, carefully formulated diets containing 16.0-16.2% crude protein, which meets requirements for the lactating cow and still provides a reasonable margin of safety, would reduce N excretion in urine by about 20% (Broderick, 2003).

Various lactation trials have been conducted whereby Holstein cows were fed different levels of CP, fiber, corn silage, alfalfa silage, alfalfa haylage, and tannin-containing forages [alfalfa, birdsfoot trefoil low tannin (BF-T-Low) and birdsfoot trefoil high tannin (BF-T-High)]. Thus far, most tested diets have had small, if any impact on milk production, or milk protein and fat content, but affected the amount and relative N partitioning between urine and feces (similar pattern to what is depicted in Figure 1; Broderick, 2003; Misselbrook et al., 2005). Increases in urine N excretion due to excessive feeding of dietary protein and/or feeding highly soluble protein increases ammonia emissions (Table 2). Fresh and stored slurry from low CP (13.6%) diet had less than one-half the ammonia loss than slurries from the high CP (19.4%) diet (Table 2). Fresh slurry derived from BF-T-High diets had less ammonia loss than slurry from alfalfa or BF-T-Low diets. Stored slurry from BF-T-High and -Low diets had less ammonia loss than slurry derived from alfalfa.

Table 2. Cumulative ammonia emissions for fresh and stored slurries derived from different dairy diets applied to silt loam soil (Misselbrook et al., 2005).

Trial type	Trial components	Liquid manure type	
		Fresh	Stored
		% applied N volatilized	
CP level	13.6%	31b[†]	12b
	19.4%	68a	29a
Forage tannin type	Alfalfa	31a	30a
	BF-T-Low	33a	23b
	BF-T-High	25b	19b

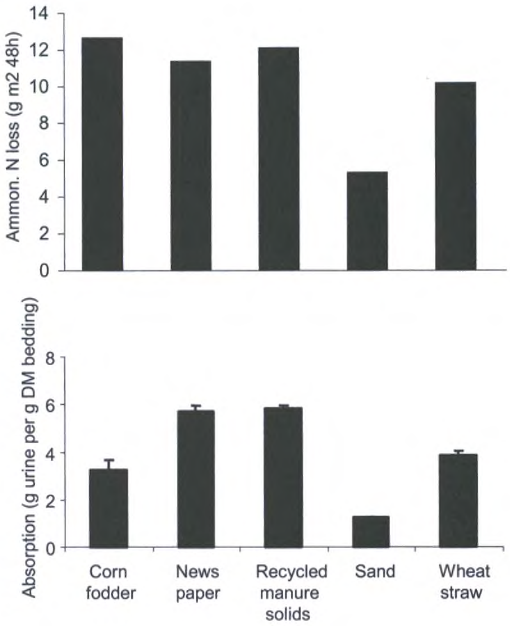
[†] within each trial, values with different letters are significantly different ($P<0.05$)

Bedding Affects Ammonia N Loss from Dairy Barns

Dairy cattle barns are thought to be major sources of ammonia emissions to the atmosphere. Our research is showing that the bedding material used can influence the magnitude of these emissions. The physical characteristics (urine absorbance capacity, bulk density) of bedding materials are of more importance than their chemical characteristics (pH, cation exchange capacity, carbon to nitrogen ratio) in determining ammonia emissions from applied urine and feces (Misselbrook and Powell, 2005). For example, of the bedding types commonly used in dairy barns, sand is the least and recycled manure solids the most urine absorbent. (Fig. 2). When equal volumes of urine were applied to dry bedding, ammonia emissions over 48 h were significantly lower from sand than from the other bedding types.

Preliminary results from in-barn trials show a similar pattern of ammonia emissions from beddings to that determined in the lab. Ammonia loss from composted manure solids was greater than from chopped straw and pine shavings (Data not shown). Because of warmer temperatures, ammonia emissions are 20 to 55% greater during the summer than during the winter. Our initial studies indicate that the selection of bedding type may be based not only on cow comfort and health, but also on their ability to reduce ammonia N emissions.

Fig. 2. Urine absorbance capacity and cumulative ammonia N emissions from different beddings (Misselbrook and Powell, 2005)



Impact of Ammonia Loss on Plant Availability of Manure Nitrogen

In areas where dairy production is integrated with crop production, ammonia loss from manure is important because it is a direct loss of crop N that is available to the farmer. Given the high potential of ammonia N loss in manure handling, storage, and land application, only a small fraction of the N excreted by a dairy cow and applied to land may actually be recycled through crops. Furthermore, the loss of ammonia N also reduces the nitrogen:phosphorus ratio in manure, which may increase the risk of manure phosphorus applications in excess of crop needs. Many dairy farms have soil test phosphorus levels that exceed agronomic recommendations, and the runoff of phosphorus from these fields and subsequent pollution of lakes, streams, and other surface waters has become a major concern.

Reducing ammonia N losses from dairy farms and making greater use of conserved manure N will quickly make economic sense. Natural gas accounts for 75-90% of the cost of making anhydrous ammonia. As the price of natural gas continues to skyrocket, the fertilizer N value of manure, and therefore the conservation of the ammonia N contained in manure, will become more important. Reducing volatile N losses would not only conserve manure N available for field applications, but also reduce the amount of carbon dioxide, a greenhouse gas, that is generated in making fertilizer N.

Conclusions

Substantial reductions in ammonia loss from dairy farms can be achieved by reducing in-barn losses, by covering manure storage, and by incorporation of manure in the field. The following steps can be a guide for action:

1. Remove excess protein from the cow's diet. This normally saves on feed cost, as well as reducing ammonia N emissions.
2. For new construction, floors that divert urine away from feces can reduce ammonia emissions. Slatted floors facilitate this, but there is still considerable loss of ammonia from the surface of the slatted floor.

3. Select bedding (e.g. sand, pine shavings) that separate feces and urine, which reduce ammonia losses.
4. Cover the manure storage. When organic bedding such as straw is used, a crust will form on the surface of the slurry pit. This reduces ammonia N losses and odors. Excessive agitation during unloading of the slurry from storage should be avoided.
5. Incorporate manure in the field. However, this strategy needs to consider potential tradeoffs in situations where nitrate leaching may be a concern.

Implementation of 1, 3, 4 and 5 could potentially reduce ammonia N loss from about 50 to 14-18 kg/cow/yr, a 65-70% reduction. This means additional 32-36 kg N per cow would be available annually for application to field crops. At a fertilizer N value of $0.75/kg N, this can mean annual savings of $2,300 to $2,700 per 100 dairy cows on fertilizer costs.

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Distortion of Turbulence in the Flow Field Surrounding an Agricultural Facility

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Abstract

The emission and dispersion of particulates from agricultural facilities at local to regional scales is a current issue in science and society. The transport of particulates in the atmosphere at these scales is largely determined by turbulence. Any models that attempt to simulate the dispersion of particles will specify or assume various statistical properties of the turbulence field. Statistical properties of turbulence are well documented for idealized boundary layers above uniform surfaces. However, an animal production facility is a complex surface with structures that act as bluff bodies and greatly distort the turbulence fields in the vicinity. As a result, the initial diffusion of plumes in the local region will be greatly affected by the complex nature of the surface. Previous LIDAR studies of plume dispersion over a facility indicate that plumes move in complex yet organized patterns that would not be explained by the properties of turbulence generally assumed in models. The objective of this study was to characterize the near surface turbulence statistics in the flow field in the vicinity of an array of animal confinement buildings. This was accomplished by erecting three towers in the upwind, within the array and downwind regions of the flow field. Changes in various turbulence statistics will be analyzed as the wind moved over the site. These include power spectra and cross-spectra, and identification of intermittent structures. The distortion of the turbulence by the structures will be quantified, as well as how it is related to various atmospheric conditions.

Introduction

The emergence of large scale animal production facilities has contributed to concerns pertaining to the impact on air quality due to the emissions of particulates, odors ammonia (NH_3), methane (CH_4) and a suite of volatile organic carbons (VOC's). The focus of this investigation is particles. Confined animal production facilities present a unique challenge to estimating transport into the surrounding atmosphere. The usual approach of eddy covariance to determine fluxes, is not valid in such cases, since underlying assumptions of extensive source regions that are flat and uniform are simply not valid in these cases. These facilities contain the additional complexity of buildings distributed in a variety of configurations that act as bluff body obstructions to the mean wind flow that will affect the turbulent transport processes. To effectively model the transport processes at such facilities, requires documentation of effects of bluff bodies (or buildings) on the turbulent flow field near the facility.

The properties of the turbulence and resultant diffusion, result from both the general state of the micrometeorological conditions that contribute to the stability of the boundary layer at the surface, and the local effects of structures present at the facility. The mechanisms of the dispersion of the particulates are governed by scales of turbulence that range from very small local scales of cm, up to the atmospheric boundary layer that may extend to heights of several km.

In order to understand the transport of particles from a complex source, such as an agricultural facility, the distortion of the turbulence by the array of sources must be documented. The effects of the structures on the turbulence must be quantified and related to the properties of the undisturbed flow field.

The objectives of this study are:

1. To quantify the changes in turbulence statistics that result from the presence of the structures and spatially complex sources of an agricultural facility.
2. Integrate these findings with the observed images of spatial variations of particle density determined from lidar measurements.

Methods

A study was conducted at a small swine facility near Ames, Iowa that began in late August and continued for 10 days into early September of 2005. The facility was comprised of three buildings with dimensions of 55 m length by 18 m wide and 6 m in height with the length of the buildings oriented in an east-west direction. They were separated by a distance of 18 m. Each building housed approximately 1300 pigs and represented the source area for particulates. At a distance of 200 m to south of the facility a 10 m tower was erected in a soybean field, with two eddy covariance systems mounted at 4 and 8 m above the soybean canopy. The same configuration was sited 200 m to the north of the buildings in a corn field. The prevailing wind direction during the study was from the S-SW, and the above towers represented upwind and downwind (from the buildings) turbulence conditions. Between the northern most and center buildings a 20 m tower was erected, onto which 3 eddy covariance systems were mounted at 7, 12 and 18 m above the ground level. The 7 m height was approximately 1 m above the apex of the building roof. This configuration allowed us the opportunity to measure horizontal and vertical turbulence characteristics of the wind flow in the upwind, among building and downwind turbulence flow fields.

Each EC system for all towers was comprised of a 3-D sonic anemometer (CSAT3, Campbell Scientific Inc.) and a LI7500 IRGA (LiCOR Inc.). Additional meteorological instrumentation included a temperature and humidity probe (HMP-45, Vaisala) on each tower. At the 20 m tower all three eddy covariance systems were wired to a single data logger (CR5000, Campbell Scientific Inc.) so that simultaneous and synchronized data acquisition could be accomplished for the vertical EC configuration. The north and south tower EC systems were also wired to a CR5000 data logger. The EC systems were programmed to sample at a rate of 10 Hz while the temperature and humidity sensors were sampled at a rate of 1 Hz. The high frequency EC data series were conditioned following common procedures in micrometeorology described in Kaimal and Finnigan, (1994).

Preliminary Results

The initial analysis of the data begin by identifying a simple case that would include strong winds from the south, to document changes in turbulence statistics upwind, over, and downwind of the facility. This occurred on September 05, 2005 between 1100 and 1600 hours. We present the ambient wind and temperature conditions for the period from 1500-1600 hours (Table 1).

Tower	*Wind speed*	*Temperature*	*Wind Direction*	u_*
	(m/s)	**(deg C)**	**(deg)**	**(m/s)**
South	5.3	29.0	197	0.40
Bottom	3.1	29.5	196	0.69
Middle	5.1	29.0	194	0.56
Top	6.1	29.8	193	0.39
North	3.0	28.7	190	0.50

Table 1. Average wind and temperature conditions for DOY 248, for the period between 1500-1600 hours at the south, north and 20 m towers.

Table 1 shows that air temperatures were warm with moderate winds originating from the south at ~ 5 m/s. Friction velocity (u_*) values ranged between 0.39 and 0.69 m/s in response to different surface roughness conditions. The largest intensity of turbulence was observed at the lowest height of the tower over the facility, likely due to the bluff effects of the buildings. Average air temperatures were coolest over the corn surface and warmest over the building array. A notable difference can be seen between the average wind speeds over the soybean (south) in the approach position relative to the corn (north) and is an indication of the greater surface roughness presented by the corn canopy relative to the soybeans.

A sample of the normalized cospectra plots for momentum (*uw*) from the three heights at the 20 m tower is shown in Figure 1. The cospectra show the contribution to the flux by eddies of different frequency. In this case we are interested in the influence of the buildings on the turbulence structure for momentum and apply this understanding to particulate transport. The upper plot corresponds to the top location on the tower and descends accordingly with the bottom plot representing the bottom eddy covariance system. The observed spectra for the three heights show a trend where the frequencies of peak contributions grow smaller with height. This is reasonable and expected as the greater heights will encounter larger eddies relative to the bottom system. However, the magnitudes of the cospectral densities are greatest at the bottom and least at the top, indicating more momentum transfer due to the distorting effect on the turbulence from the physical building obstruction.

Note also that the reduction of the contributions at higher frequencies than the peaks, differ from the three heights. The classic 5/3 law is not observed at all heights, suggesting again the distortion of turbulence by the facility. Further analysis will examine the effects of these distortions to the H_2O and CO_2 fluxes as well as compare the cospectra results from the 20 m tower to those from the upwind and downwind turbulent fields.

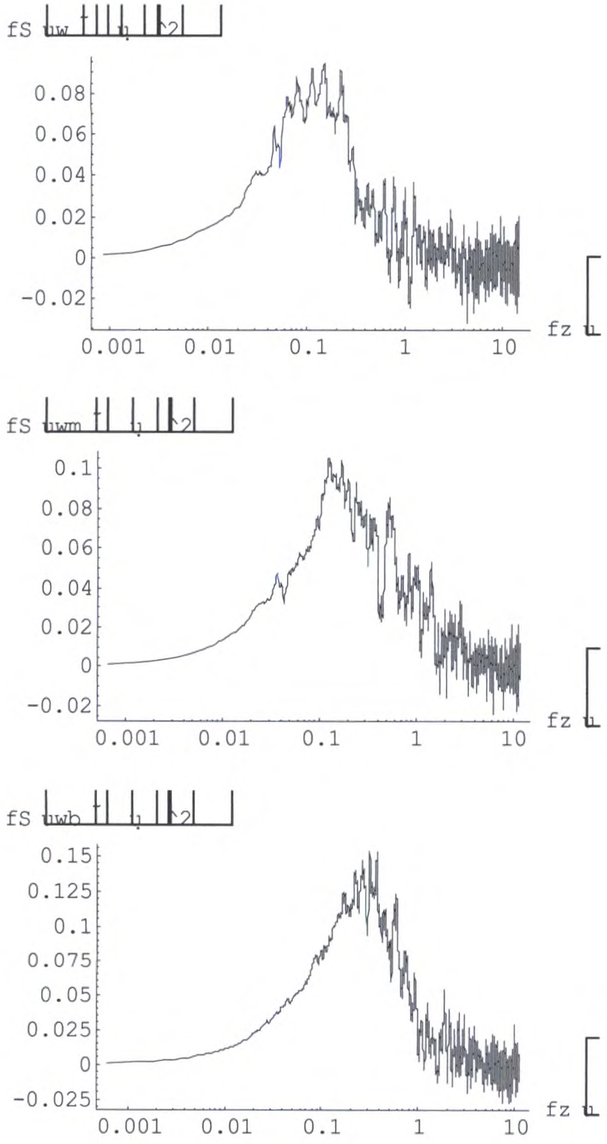

Figure 1. Cospectra of horizontal and vertical velocity for 18 m height (upper), 12 m height (middle), and 7 m height (lower), above the facility.

Future analyses will integrate the observed changes in the spectra and cospectra of turbulence, with the spatial patterns of particulates as measured by the lidar. The combination of the two sets of data will suggest how the dispersion of particulates is affected by the complexity of such a site. The results will suggest implications for modeling the dispersion of particles from these facilities.

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Impact of Precipitation Physics on CMAQ Wet Deposition Predictions

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Abstract

Precipitation aids the natural removal of atmospheric pollutants through the process of wet deposition. This process affects the ambient pollutant concentrations along with the amount and chemical composition of ground-level precipitation. Because of the direct linkage between meteorological conditions and types and amounts of atmospheric constituents in precipitation, an accurate representation of meteorological fields is vital for accurate simulations of wet deposition of chemical species by air quality models (AQMs). In this work, performance evaluation is conducted for both meteorological and chemical predictions for August and December 2002 using the Pennsylvania State University (PSU)/National Center for Atmospheric Research (NCAR) Mesoscale Model Generation 5 (MM5)-the U.S. EPA Community Multi-scale Air Quality (CMAQ) modeling system. To understand the uncertainties in simulating precipitation and wet deposition, the evaluation focuses on several most influential parameters including cloud fractions, precipitation, and mass concentrations and wet deposition amounts of sulfate, nitrate and ammonium. Results from the preliminary evaluation of the August baseline simulation show overpredictions of the precipitation, cloud fraction, and wet deposition amounts and underpredictions of the PM concentrations. The December baseline simulation results show overprediction of PM mass concentrations and wet deposition of NH_4^+ and NO_3^-, and both over and underprediction of SO_4^{2-} depending on the observations used in the model evaluation. Both precipitation and cloud fraction are underpredicted by MM5 in December. Sensitivity simulations of MM5 using an alternate cloud microphysics scheme are also performed. The preliminary evaluation of the sensitivity simulation for August 2002 shows an improved model performance for precipitation. Further analysis and additional sensitivity simulations are being conducted to identify major uncertainties in simulating precipitation with MM5 and wet deposition with CMAQ.

Introduction

Air pollution can cause adverse effects on human health and well-being. One control of the amount of atmospheric pollutants is their removal via natural processes. Clouds and precipitation play a critical role in the removal of atmospheric pollutants via wet deposition processes. These removal processes can proceed first with the cloud droplet formation via several mechanisms including heterogeneous nucleation (Iribarne and Cho, 1988; Hallberg et al., 1997; Andronache, 2004) and aerosol activation (Zhang et al., 2002); then with in-cloud scavenging by existing cloud droplets (Hallberg et al., 1997; Andronache, 2004); or below-cloud scavenging by falling precipitation (Andronache, 2004) or both. All of these processes influence the amount and composition of the ground-level rainwater. Therefore, an accurate representation of clouds, precipitation, and cloud scavenging processes is necessary for three-dimensional (3-D) air quality models to realistically simulate the removal of pollutants via wet deposition. An additional intricacy in accurately simulating wet deposition lies in the fact that it depends not only the aforementioned meteorological processes/parameters but also the ambient concentrations of depositing species in both the gas- and the particulate-phase, which are in turn affected by many atmospheric processes such as emissions, transport, gas and aqueous-phase chemistry, aerosol thermodynamics and dynamics, cloud processing of aerosols, as well as dry and wet removals. The model performance for wet deposition and associated uncertainties cannot be fully assessed without examining all these important aspects.

Recent studies have shown sensitivity of the simulated meteorological variables to cloud microphysics schemes (Gilmore et al., 2004; Medaglia et al., 2005). Different microphysical treatments in those schemes can directly affect simulated clouds, precipitation, and wet deposition amounts. The impact of the associated model errors in representing cloud microphysics on simulated wet deposition cannot be well understood without assessing the appropriateness of those schemes and the importance of model biases in meteorological predictions relative to those in chemical predictions. The main objective of this work is to study major uncertainties in the simulated wet deposition amounts of ammonium (NH_4^+), nitrate (NO_3^-), and sulfate (SO_4^{2-}) using the Pennsylvania State University (PSU)/National Center for Atmospheric Research (NCAR) Mesoscale Model Generation 5 (MM5)-the U.S. EPA Community Multi-scale Air Quality (CMAQ) modeling system. This objective is achieved by first evaluating the impacts of cloud microphysics schemes used in MM5 on the predicted wet deposition amounts through influencing the simulated clouds and precipitation, and then by evaluating the impact of model biases in the simulated PM concentrations on the wet deposition predictions through influencing the amounts of PM available for wet removal. The two types of evaluations involve the use of observational data for meteorological variables such as cloud fractions and precipitation and chemical quantities such as mass concentrations and wet deposition amounts of PM species (e.g., NH_4^+, NO_3^-, and SO_4^{2-}). As the first step, this study examines the performance of MM5/CMAQ with the default cloud microphysics scheme (i.e., the Reisner 1 scheme) in reproducing two meteorological parameters (i.e., cloud fractions and precipitation) and two chemical quantities (i.e., mass concentrations and wet deposition amounts) and the sensitivity of cloud fractions and precipitation to an alternate cloud microphysics scheme (i.e., the Reisner 2 scheme) used in MM5. Of particular interest to this study is the model performance on predicting the wet deposition of particulate species potentially affected by agricultural emissions of ammonia (NH_3), including NH_4^+, NO_3^-, and SO_4^{2-}, due to the dominancy of agricultural sources in the total NH_3 emissions in the simulation domain of interest (i.e., the state of North Carolina (NC)).

Methods

The study uses the MM5 version 3.7 simulation as input for CMAQ version 4.4. The MM5 simulations are conducted with four-dimensional data assimilation (FDDA) analysis. 3-D analysis nudging is performed for temperature and moisture aloft, and both 3-D and surface analysis nudging are conducted for wind fields. The meteorological output was translated for use in CMAQ by the Meteorology-Chemistry Interface Processor (MCIP). This modeling system is applied for two one-month simulations (August and December 2002) with a 4-km horizontal grid spacing over a domain covering most of NC and portions of the surrounding states. Figure 1 shows the modeling domain with a 4-km horizontal grid spacing and the locations of the measurement sites from all monitoring networks used in the model evaluation. The names of those sites and the associated networks are given in Table 1. The simulations are initialized using initial and boundary conditions generated from the Visibility Improvement State and Tribal Association of the Southeast (VISTAS) 12-km MM5 and CMAQ simulations. No additional spinup is therefore conducted to reinitialize the 4-km simulations. For the baseline simulation, the modeling configurations are kept to be the same as those for the 12-km resolution simulations. For example, the CBM-IV mechanism is used to simulate gas-phase chemistry and the aero3 module is used to simulate aerosol dynamics in CMAQ. More details of model configurations can be found in the modeling protocol for the VISTAS Phase II regional haze modeling (Morris and Koo, 2004). It is important to note that at the 4-km grid resolution, the clouds from the MM5 cumulus parameterizations are not included in the CMAQ cloud module. This adjustment is made based on the assumption that the subgrid-scale clouds, which are parameterized in the cumulus schemes are resolved at 4-km (Roselle and Binkowski, 1999). The baseline CMAQ simulations use MM5 input files generated with the mixed phase (Reisner 1) microphysics scheme. Additional sensitivity simulations for both months are being completed with an alternative microphysics scheme (Reisner 2) that separately considers graupel and riming processes (Reisner et al., 1998).

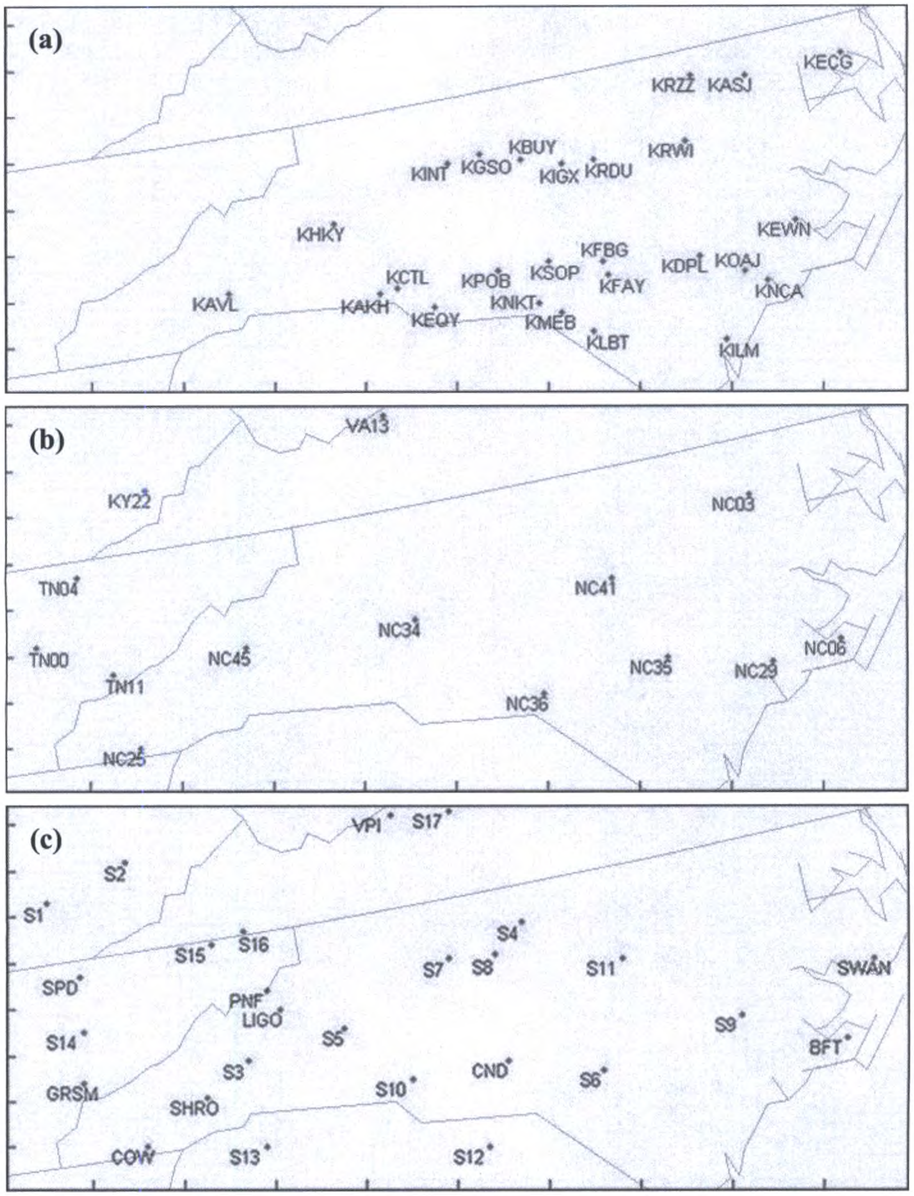

Figure 1. Modeling domain with a 4-km horizontal grid spacing and the locations of measurement sites from (a) ASOS/AWOS, (b) NADP, and (c) IMPROVE, STN, and CASTNet used in the model evaluation. The full names and locations of all measurement sites and their associated networks are given in Table 1.

The simulated fields that are evaluated include 8 parameters, namely, hourly cloud fraction, weekly total precipitation, weekly total wet deposition of NH_4^+, NO_3^-, and SO_4^{2-}, and daily averaged particulate matter (PM) concentrations of NH_4^+, NO_3^-, and SO_4^{2-}. Observational data from six monitoring networks are used for model evaluation. These networks include the NC Automated Surface Observation Systems (ASOS), the Automated Weather Observing System (AWOS), the National Acid Deposition Program (NADP), the Clean Air Status and Trends Network (CASTNet), the Interagency Monitoring of Protected Visual Environments (IMPROVE), and the Speciated Trends Network (STN). Table 2 summarizes the total number of sites and sampling times of all observational data and their associated networks that are currently used in this study. The simulated hourly cloud fraction values taken from MCIP are compared with the ASOS and AWOS hourly observations. Only 26 total ASOS and AWOS sites out of a total of 60 NC sites are included in the model evaluation because of the availability of continuous datasets during

August and December 2002. The remaining sites are excluded because of significant data missing. The weekly precipitation calculated from MCIP and the weekly wet deposition predicted by CMAQ are compared with the weekly NADP observations. Observational datasets from CASTNet, IMPROVE, and STN are used to evaluate model performance for concentrations of PM species in terms of statistical analyses, and temporal and spatial variations.

Table 1. The full names and locations of all 68 measurement sites and their associated networks.

Site ID	Site Name	Network	Latitude	Longitude
KAKH	Gastonia Municipal Airport	ASOS	35.2	-81.1
KAVL	Asheville Regional Airport	ASOS	35.4	-82.5
KBUY	Burlington Alamance Airport	ASOS	36.0	-79.5
KCTL	Douglas International Airport	ASOS	35.2	-80.9
KECG	Coast Guard Air Field	ASOS	36.3	-76.2
KEQY	Monroe Airport	ASOS	35.0	-80.6
KEWN	Craven County Airport	ASOS	35.1	-77.0
KFAY	Fayetteville Airport	ASOS	35.0	-78.9
KGSO	Greensboro Airport	ASOS	36.1	-79.9
KHKY	Hickory Airport	ASOS	35.7	-81.4
KIGX	Chapel Hill-Williams Airport	ASOS	35.9	-79.1
KILM	New Hanover County Airport	ASOS	34.3	-77.9
KINT	Smith Reynolds Airport	ASOS	36.1	-80.2
KLBT	Lumberton Municipal Airport	ASOS	34.6	-79.1
KMEB	Laurinburg-Maxton Airport	ASOS	34.8	-79.4
KRDU	Raleigh-Durham Airport	ASOS	35.9	-78.8
KRWI	Rocky Mount-Wilson Airport	ASOS	35.9	-77.9
KRZZ	Halifax County Airport	ASOS	36.4	-77.7
KASJ	Tri-County Airport	AWOS	36.3	-77.2
KDPL	Duplin County Airport	AWOS	35.0	-78.0
KFBG	Simmons Army Airfield	AWOS	35.1	-78.9
KNCA	New River MCAS	AWOS	34.7	-77.4
KNKT	Cherry Point MCAS	AWOS	34.9	-76.9
KOAJ	Albert Ellis Airport	AWOS	34.8	-77.6
KPOB	Pope AFB	AWOS	35.2	-79.0
KSOP	Moore County Airport	AWOS	35.2	-79.4
KY22	Lilley Cornett Woods	NADP	37.1	-83.0
NC03	Lewiston	NADP	36.1	-77.2
NC06	Beaufort	NADP	34.9	-76.6
NC25	Coweeta	NADP	35.1	-83.4
NC29	Hofmann Forest	NADP	34.9	-77.3
NC34	Piedmont Research Station	NADP	35.7	-80.6
NC35	Clinton Crops Research Station	NADP	35.0	-78.3
NC36	Jordan Creek	NADP	35.0	-79.5
NC41	Finley Farm	NADP	35.7	-78.7
NC45	Mt. Mitchell	NADP	35.7	-82.3
TN00	Walker Branch Watershed	NADP	36.0	-84.3
TN04	Speedwell	NADP	36.5	-83.8
TN11	Great Smoky Mountains National Park-Elkmont	NADP	35.7	-83.6
VA13	Horton's Station	NADP	37.3	-80.6

S1	21-125-0004	STN	37.1	-84.1
S2	21-193-0003	STN	37.3	-83.2
S3	37-021-0034	STN	35.6	-83.4
S4	37-033-0001	STN	36.3	-79.5
S5	37-035-0004	STN	35.7	-81.4
S6	37-051-0009	STN	35.0	-79.0
S7	37-067-0022	STN	36.1	-80.2
S8	37-081-0013	STN	36.1	-79.8
S9	37-107-0004	STN	35.2	-77.6
S10	37-119-0041	STN	35.2	-80.8
S11	37-183-0014	STN	35.9	-78.6
S12	45-025-0001	STN	34.6	-80.2
S13	45-045-0009	STN	34.9	-82.3
S14	47-093-1020	STN	36.0	-83.9
S15	47-163-1007	STN	36.5	-82.5
S16	51-520-0006	STN	36.6	-82.2
S17	51-770-0014	STN	37.3	-80.0
GRSM	Great Smoky Mountains NP	IMPROVE	35.6	-83.9
LIGO	Linville Gorge	IMPROVE	36.0	-81.9
SHRO	Shining Rock Wilderness	IMPROVE	35.4	-82.8
SWAN	Swanquarter	IMPROVE	35.5	-76.2
VPI	Horton Station	CASTNet	37.3	-80.6
COW	Coweeta	CASTNet	35.1	-83.4
PNF	Cranberry	CASTNet	36.1	-82.0
BFT	Beaufort	CASTNet	34.9	-76.6
SPD	Speedwell	CASTNet	36.5	-83.8
GRS	Great Smoky NP-Look Rock	CASTNet	35.6	-83.9
CND	Candor	CASTNet	35.3	-79.8

Given different sampling time resolutions for the observed variables, different time scales are used for comparison of simulated concentrations of PM species against those obtained from the three networks and for comparisons of simulated cloud fractions and precipitations. While the use of different time scales ensures statistical calculations paired with time and space for individual variable from individual network, it, however, creates difficulties and uncertainties in the cross-comparison of variables with inconsistent time scales from different networks. For example, the bias in predicting hourly cloud fractions from ASOS/AWOS is difficult to be linked to the bias in the predicted weekly total precipitation. Similarly, the bias in predicting 24-hr averaged concentrations of PM species (observed values are available every three days) from STN and IMPROVE is difficult to be interpreted to quantitatively indicate the bias associated with the weekly total amounts of PM species available for wet deposition amounts that are measured as a weekly total from NADP. While the hourly precipitation dataset from the national weather service (NWS) are being acquired and will permit a cross-comparison with hourly cloud fractions, we also calculate the monthly-averaged statistics to partially address this temporal inconsistency, in addition to statistics at different time scales. Lack of spatially-collocated datasets presents another limitation, also making the site-specific comparisons difficult. A careful interpretation of statistics obtained for different parameters at different sites is thus warranted. One approach to potentially address the spatial inhomogeneity is to perform additional evaluations (such as time series comparisons of different parameters and site-specific statistics) by grouping data from sites with similar site characteristics and/or within a distance of proximity (e.g., coastal vs. inland, rural vs. urban, upwind vs. downwind). Nevertheless, despite the sparseness or unavailability of collocated dataset for parameters paired up in space and time across all networks during the simulation period for the domain of interest, the cross-comparisons with different time scales and with monthly-averaged statistics may more or less provide qualitative (if not semi-quantitative or quantitative) linkages among different parameters and may help identify critical data need for a more rigorous model evaluation.

Table 2. Observational datasets used for the model evaluation.

Network	Parameter/Species		Total Sites Evaluated	Sampling Period
ASOS/AWOS	MET	Cloud Fraction	26	Instantaneous hourly
NADP	MET	Precipitation	14	Weekly total
	WETDEP	NH_4^+, NO_3^-, SO_4^{2-}	14	Weekly total
CASTNet (mostly rural sites)	PM	NH_4^+, NO_3^-, SO_4^{2-}	7	Weekly average
STN (urban areas and towns)	PM	NH_4^+, NO_3^-, SO_4^{2-}	17	1in 3 days; 24-hour average
IMPROVE (mostly remote sites)	PM	NH_4^+, NO_3^-, SO_4^{2-}	4	1 in 3 days; 24-hour average

The performance statistics calculated for all eight parameters include both the traditional measures such as the correlation coefficient (*r*), the mean bias (MB), the mean absolute gross error (MAGE), the root mean squared error (RMSE), the mean normalized bias (MNB), the mean normalized gross error (MNGE), the normalized mean bias (NMB), the normalized mean gross error (NMGE), the fractional bias (FB), and the fractional gross error (FGE) and the new statistical metrics developed by Yu et al. (2003) such as the mean normalized factor bias (MNFB), the mean normalized gross factor error (MNGFE), the normalized mean bias factor (NMBF), and the normalized mean error factor (NMEF). These metrics are calculated over the entire month for the entire domain based on individual observation-model data pairs for all eight parameters using observation time scales from each network. The use of observational data for the concentrations and wet deposition amounts of PM species from three different networks for separate statistical calculations provides a range of statistics for the three networks. In addition to evaluation at observation time scales, statistics are calculated for the monthly averaged observation-modeled data pairs for cloud fractions, precipitation, and wet deposition amount to reduce the influence of different sampling periods of raw data. Monthly-averaged statistics for PM concentrations are not evaluated, however, because of the relatively small number of sites from IMPROVE and CASTNet (4 and 7, respectively). For monthly statistics, all data pairs are averaged over the month at each individual site and the domain-wide statistics are then calculated from the monthly averages at all sites. Preliminary evaluation results with monthly-averaged statistics and those averaged at the observation time scales (i.e., hourly to weekly) are discussed in the following section.

Results and Discussions

Preliminary evaluation for the August baseline MM5 simulation shows that the simulated meteorological parameters are typically not in strong agreement with observed values. For example, the correlation of the simulated and observed weekly total precipitation amounts was weak with a correlation coefficient (*r*) value of 0.34 (0.39). Simulated and observed hourly cloud fractions during August are in better agreement with an *r* value of 0.49 (-0.10 for monthly-average). However, both meteorological parameters show moderate model overpredictions, with NMBs of 40.93% (40.95% for monthly-average) and 38.56% (37.71% for monthly-average) for precipitation and cloud fraction, respectively. Meanwhile, the baseline CMAQ simulation shows overall underpredictions for mass concentrations of all three PM species during the month of August with varying correlation coefficient values based on the location and network of the sites. Correlations between the predicted and observed values of PM mass concentrations of NH_4^+ and SO_4^{2-} are relatively high with values for the three networks ranging from 0.61-0.81 and 0.51-0.86, respectively. Overall, CMAQ significantly overpredicts the weekly total wet deposition of all three species during August, with NMBs of 153.1% (154.7% for monthly-average) for NH_4^+, 23.4% (26.1% for monthly-average) for NO_3^-, and 363.5% (367.3% for monthly-average) for SO_4^{2-}. The large values of NMB are due to large overpredictions of the wet deposition of NH_4^- and SO_4^{2-} during the first week of August, during which the observed values were small, but the modeled values were significantly higher. The model performance for the wet deposition amounts of NH_4^+ varies both temporally and spatially with most sites having both over- and under-prediction during August. Wet deposition predictions of SO_4^{2-} are also highly variable; in some cases, especially those with low observed SO_4^{2-} values, the predictions are more than twice the observed amounts. Although domain-wide statistics reflect overpredictions of NO_3^- wet deposition amounts, spatial variations do occur with some sites having modeled values that are 50% or less of the observed values. As shown above, small differences exist between the monthly NMBs and those with the observation time scales for precipitation, cloud fraction, and wet deposition amounts of all species and *r* for precipitation. However, the correlation between observed and modeled values of cloud fractions on an hourly basis is higher by a factor of 5 than that on a monthly-average basis. Examination of data pairs shows that monthly-averaged hourly simulated cloud fraction values for all sites range 0.42 to 0.50 compared to a range of 0.17 to 0.65 monthly-averaged hourly observed cloud fractions. Values for both observed and simulated individual cloud fraction range from 0.00 to 1.00. Thus, with a limited range of simulated values, the correlation coefficient for the monthly-average cloud fraction values is significantly smaller than that of the individual cloud fraction values.

The preliminary evaluation of the December baseline simulation shows overpredictions of both weekly precipitation and hourly cloud fraction. The calculated correlation coefficients for both parameters are better during this month than during August, with values of 0.52 and 0.36 for weekly total and monthly average precipitation, and 0.71 and 0.17 for hourly and monthly average hourly cloud fraction. The December CMAQ baseline simulation results show a weak correlation between simulated and observed wet deposition values, with values of *r* ranging from -0.06 to 0.25 for weekly total and -0.15 to 0.42 for monthly averaged wet deposition amount. Overpredictions of wet deposition amounts occur for all three species, with NMBs of 109.1% (111.4% for monthly average) for NH_4^+, 109.3% (106.9% for monthly-average) for NO_3^-, and 66.9% (66.3% for monthly-average) for SO_4^{2-}. Correlation coefficients calculated using weekly total and monthly averaged values for both NO_3^- and SO_4^{2-} are similar, but differ largely for NH_4^+ *r* values (0.25 vs. 0.42, respectively). Observed and simulated PM mass concentrations have stronger correlations than those for wet deposition, with values of *r* from the three observational networks in the ranges of 0.51-0.64, 0.48-0.73, and 0.45-0.46 for NH_4^+, NO_3^-, and SO_4^{2-}, respectively. Both NH_4^+ and NO_3^- are overpredicted during December, while either overprediction or underprediction may occur for SO_4^{2-} depending on the network. While the *r* values obtained with monthly average and the observation time scales (e.g., hourly or weekly total) for both cloud fraction and precipitation in December show larger difference than those in August, the NMBs for both evaluation methods remain very similar. The differences in statistics based on monthly averaged and weekly total are small for wet deposition amounts during December. Similar to the comparison for August, the largest difference in the statistical values calculated based on the two different time scales is found in the cloud fraction correlations. During December, correlation coefficients that are based on monthly averaged values for cloud fractions are nearly 5 times smaller than those based on hourly. Similar to results in August, the range of simulated values for the monthly-average cloud fraction (0.33-0.40) is much narrower than that of the simulated individual cloud fraction values (0.00-1.00). This shrinking in the range of simulated cloud fraction explains the large reduction in the correlation coefficient for monthly-average cloud fraction values.

A preliminary comparison between the MM5 baseline and sensitivity simulations for August 2002 has been conducted. Simulated total cloud fraction does not change significantly in the sensitivity simulation, because the cumulus cloud scheme is turned off in the 4-km simulation. The correlation coefficients based on hourly data remain similar for the sensitivity simulation with only a slight increase of the NMB from 38.6% to 39.1%. However, the sensitivity simulation with the Reisner 2 scheme does show significant improvement in the simulated precipitation during August, changing a moderate overprediction with an NMB of 40.9% in the baseline simulation to a slight underprediction with an NMB of -3% in the sensitivity simulation. The statistics based on monthly average and the observation time scales for the two parameters predicted by the sensitivity simulation are similar to those of the baseline simulation. NMBs for both precipitation and cloud fraction have only slight differences. However, correlation coefficients based on different time scales for both parameters are quite different. The values of *r* are 0.42 and 0.50 for weekly total precipitation and hourly cloud fraction, respectively while the values are 0.23 and -0.08, for monthly averaged precipitation and cloud fraction, respectively.

The baseline simulations for August and December will be further evaluated in terms of temporal and spatial variability. Further analysis is being conducted to understand mechanistically the differences between the MM5 baseline and the sensitivity simulation results using different cloud microphysics schemes. Sensitivity simulations of CMAQ for August (and December, if justified) will be conducted using the meteorological fields from the MM5 sensitivity simulations with the Reisner 2 microphysics scheme.

These results will then be compared with those from the baseline simulation to examine the impacts of alternate MM5 microphysics schemes on the wet deposition predictions by CMAQ. Additional diagnostic and sensitivity simulations may also be conducted to identify other possible reasons for differences between observed and simulated wet deposition amounts.

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Brickmaking in Agricultural Communities in Mexico: Distribution, Fuels Inventory, Emissions, and Effects on Animals and Plants

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Abstract

Rural agricultural communities in the state of Queretaro (Qro.), in the central highlands of Mexico, are often sites of co-located industrial activities to supplement farm income. Notable among these are small-scale brickmaking operations, unlicensed and unregulated, highly contaminating, and located in close proximity to human habitations, field and permanent crops, and domesticated animals. Although small when considered individually, these industrial activities may dominate air quality degradation in these rural areas (Blackman, 2000). These brick kilns are characterized by inefficient combustion of extremely polluting fuels of many types. Similar situations exist in many developing countries, where brickmaking is well established as a significant source of hazardous gaseous and particulate pollutants. Areas of influence of individual brick kilns and of groups of kilns depend on transport and deposition characteristics of the emissions. Magnitudes and risks of exposure depend on the composition of emissions, the relative locations of sources and sensitive sinks, and access to the human food chain. These remain poorly characterized for these agricultural communities. Here we report a multi-scaled analysis of these problems. We have conducted a spatial analysis of the entire state of Queretaro, using GIS and GPS technologies, of the co-location of brick kilns, agricultural fields, exposed human populations, operator-reported fuel inventories, and brick making capacity. We have further characterized the small community of San Nicolas, Tequisquiapan, which exhibits a particularly dense and co-mingled distribution of kilns, crops and human dwellings, and represents 72% of the nearly 500 kilns in the state of Qro. Here we have defined wind patterns, established zones of influence of individual and aggregate sources, determined fuel inventories, and documented the spatial relationships among crop species, population densities and kiln locations. We have obtained photographic evidence of the density of plumes and samples of airborne and soil-deposited particles for gravimetric and chemical characterization. In this community we have determined some biological impacts of emissions on non-domesticated receptor mammals trapped in the wild (field mice: *Myotis spp*), by evaluation of genetic damage in peripheral blood cells using the micronucleus and comet assays. Further work is planned on deposition to vegetation and contamination of grain crops. Our results to date indicate that the human populations of these agricultural communities are at considerable risk of direct exposure to airborne contaminants, and that these contaminants are likely to enter the food chain through exposed crops and domesticated animals, potentially affecting urban populations. In these rural communities agricultural air quality is less impacted by traditional sources of agriculturally-sourced emissions than by co-located primary industries such as brickmaking. The results indicate that the emissions are biohazardous at current exposure levels. In the state of Queretaro, Mexico, approximately 200,000 rural inhabitants may be directly impacted.

Introduction

Agriculture and air quality exhibit many interactions, with effects in both directions. Agricultural communities have traditionally engaged in a variety of light industrial activities to supplement farm income. In these ways, the rural agricultural communities of the state of Querétaro, central highlands of Mexico, are typical. They are often sites of co-located, small-scale brickmaking operations situated in close proximity to human habitations, plantings of a variety of field and permanent crops, and domesticated animals cultivated for meat, milk, and wool.

Figure 1. A) Typical co-location of brick kiln, fuel oil supply, and residential compound. B) The fuel feeding system and open hearth of a kiln in San Nicolas.

The brick-making installations provide a dominant source of income in some of these communities. The facilities and artisanal knowledge are handed down through the generations. The bricks are traditionally sun-dried then baked in kilns to produce the required mechanical strength and characteristic red color. A typical oven produces about 10,000 bricks per month, enough to construct about 3.5 typical (22.5 m^3) rooms. However, their copious 'stack' emissions to the air (Fig. 1A), their proximity to sensitive receptors, and the unknown nature of transport, deposition and chemical composition of the emissions, have raised serious questions about the sustainability of these agricultural-industrial-residential complexes.

The kilns are built of the locally-made bricks, measuring approximately 27 to 64 m^3, with an open top some 1.5 -2.0 m above ground, and a base excavated some 1.5 -2.0 m below ground (Fig. 1B). An opening of approximately 50 x 50 cm at below ground level in one wall allows entry of air, and introduction of fuel and water through a locally constructed burner device that introduces a drip of liquid fuel and vaporized water. The burner consists of a piece of U-shaped iron pipe, with separate pressure fittings to allow entry of water and fuel. The water enters through a one-way valve, so that it becomes pressurized in the kiln and is injected alongside the fuel to disperse it throughout the firebox (bottom of Fig. 1B).

Figure 2. A field of grain sorghum nearing harvest in San Nicolas.

A typical brick kiln in the village of San Nicolas, Tequisquiapan, Querétaro is typical of this close association, with residential compounds at right and in the rear (Fig. 1A). Nearby are agricultural fields of sorghum (*Sorghum bicolor* L. (Moench)) and other seasonal crops (Fig. 2). With rough seed heads, the S*orghum* seems likely to represent an efficient scavenger of particulate emissions.

The kilns are characterized by inefficient combustion of mixed and often extremely polluting fuels (Fig. 1B; Table 1). Liquid fuel may consist of fuel oil, recycled oil or industrial solvents. In other cases, solid fuel is loaded into the kiln, prior to loading the bricks, and manually through the lower opening during firing. Originally this solid fuel was wood, but in more recent industrial times, this has included a wide range of inexpensive, generally waste or recycled materials (Table 1), including garbage, construction waste, cloth and any other combustible that can be obtained economically.

Although there are regional technological differences in kiln design, similar situations exist in other areas of Mexico and in many developing countries, where brickmaking is well established as a significant source of hazardous gaseous and particulate air pollutants. There has been considerable research into the emissions from similar kilns near the U.S.-Mexican border (TCEQ, 2000), the Indian subcontinent (Devkota and Neupane, 1994; CIDA, 2002), and elsewhere. It has been estimated that a Mexican brick kiln fired with wood emits to the environment approximately 390 kg of pollutants per firing, including NOx (4.8 kg), CO (280 kg), particulate matter (45 kg) and volatile organic compounds (62 kg) (TCEQ, 2002). The number of brick kilns in Mexico is unknown, except for the reportedly 350 in the Texas-Mexico border (Blackman at al., 2000) and the data for Queretaro state reported below.

Table 1. The range of fuels used in the manufacture of bricks.

Recycled Oil
Fuel Oil
Filter cake from waste water treatment plants
Residual solids from municipal waste
Wax (natural and synthetic)
Used Tires
Plastic waste
Uncharacterized industrial waste from the local industry
Animal manure
Wood dust
Cloth (natural and synthetic fibers)
Construction debris
Refrigerator Insulation

There have been recent efforts (Marquez, 2001) to develop more efficient kilns with correspondingly reduced air emissions. At the present time, the MK kiln appears to be the most promising of these designs (Marquez, 2001); a 54% reduction of emissions has been demonstrated in some cases (TCEQ, 2002). A few models of such kilns are planned for installation in San Nicolas as a demonstration project.

Areas of influence of individual brick kilns and of groups of kilns depend on transport and deposition characteristics of the emissions. Magnitudes and risks of exposure depend on the relative locations of sources and sensitive target sinks, environmental transfer and access to the human food chain, and the chemical characteristics of the deposited emissions. These factors all remain poorly characterized for the agricultural communities of Querétaro, leaving the nature and magnitude of this environmental threat unknown.

The objective of the present preliminary study was to establish the first geospatially referenced inventory of brick making kilns in the state of Querétaro, along with associated information regarding the human and material resources that are devoted to this industry and current methods of kiln operation, including the actual mix of fuels being consumed. Additional objectives were to estimate the magnitude of air pollution and the biological impacts on animals, plants, and humans, and an assessment of the human population that is likely to be directly exposed. We present a multi-scaled analysis of these problems.

Methods

Geo-Referenced Inventory

A member of our team visited every brick kiln in the state of Querétaro, located its position by hand held GPS, and interviewed the brickmakers (owners or operators). These locations were plotted on a topographic map of the state (1:20,000) obtained from the National Institute of Statistics, Geography and Informatics (Instituto Nacional de Estadística, Geografía e Informática) using ArcView v. 3.2. Metadata were appended with additional site information. Population data were obtained from the Mexico National Census, 2000, and from the Mexican National Municipal Information System (INAFED, 2005).

Survey of Brickmaking Operations

A survey was developed, and delivered orally to the brickmakers at the time of each visit. Information was obtained regarding raw materials used, number and characteristics of persons employed, methods of production, kiln characteristics, production capacity, and self-identified health problems. Data averaging and projections were based on all available survey data, though some respondents did not yield usable survey data.

Micrometeorological Measurements

Basic micrometeorological information was obtained for San Nicolas, the most important brickmaking village in Querétaro. Meteorological stations (Davis Instruments) were established at three points on the periphery of San Nicolas. Meteorological information was collected every 10 minutes. Wind roses were generated using the WRPLOT View v. 5.2.1 software (Lakes Environmental).

Biological Effects

Trapping of wild rodents. Sherman traps were placed in locations 0.1 –1 km from the periphery of San Nicolas in the direction E-SE to W to capture indigenous mice. The traps were left at the location for 24 hours to cover one period of darkness. Control mice were captured similarly, at the ecological reserve of El Tángano, Qro. Mice were anaesthetized at the site of capture with chloroform, and peripheral blood (50 ul) drawn under aseptic conditions from the lateral vein in the tail. Blood was immediately mixed with heparin to prevent coagulation. All mice were then released to the wild. The capture, handling of mice, and sample collection, were performed in a manner to minimize stress to the animal.

Micronuclei assay. Five micro liters of heparinized blood were extended on clean microscope slides. The slides were air dried (24 hr) and stained as reported by Salomone et at. (1980). Briefly, slides were fixed with absolute methanol (5 min), air dried (24 hr), stained with Giemsa stain (15 min), washed and stained with Harris Hematoxylin (10 min). After washing and air-drying, the slides were analyzed under the microscope (100x) and the number of micronuclei in 2,000 erythrocytes scored. Statistical significance between means was assessed using a t test.

Alkaline single cell-gel electrophoresis (comet) assay. DNA breaks were detected as described by Singh et al. (1988). Ten microliters of heparinized blood were mixed with phosphate buffered saline (1 ml), centrifuged (3000 rpm, 5 min) and the supernatant removed. The cell pellet was re-suspended in 300 μl of 0.5% low melting point (LMP) agarose at 37ºC, and an aliquot (120 μl) was applied over a microscope slide coated with 1% normal melting point agarose. After solidification, a second layer (100 μl) of LMP agarose was applied. The cells were lyzed (2.5M NaCl, 100mM EDTA, 1% triton x-100, 10% dimethyl sulfoxide, pH 10) at 4 ºC for 1 h in the dark, exposed to alkaline conditions (300 mM NaOH, 200 mM EDTA pH 13) for 30 min, washed and electrophoresed (300 mA, 25 V) for 30 min using alkaline electrophoresis buffer (1300 mM NaOH, 200 mM EDTA pH 13). After electrophoresis, the slides were neutralized with Tris buffer (pH 7.5) and stained with ethidium bromide, and the overall comet length (CL) and comet head size (CHS) measured using a fluorescence microscope (Carl Zeizz 50HB). One hundred cells images were analyzed per mouse. Two microscope slides were used in every case to analyze one hundred cells. The comet tail length was calculated as the difference between the CL and the CHS. Cells were considered normal when comet tail length was within ±10% of CHS. The comet tails of exposed and control groups were compared using the Wilcoxon rank-sum test.

Results and Discussion

Queretaro, Statewide Scale

Kiln location. In the state of Querétaro there are currently 547 brick kilns (9% inactive) involved in the artisanal manufacture of red bricks (Fig. 3). Of these, 97.8% (535) are located in the villages or municipalities of Tequisquiapan (49.7%), San Juan del Rio (22.5%), Querétaro (15.4%) and El Marqués (10.2%). The rest (2.2%) are located in the municipalities of Pedro Escobedo (2%) and Ezequiel Montes (0.2%). The most important brickmaking community in the state is San Nicolás, a village within the municipality of Tequisquiapan. This community (Fig. 4) contains 251 kilns, 92% of the total number in Tequisquiapan and about 46% of the total number in the state. The corridor of 18 km between Tequisquiapan and San Juan del Rio (the communities of Bordo Blanco, San Nicolas, Vistha and San Pedro Ahuacatlan; Fig. 3) contains 72.2 % (395) of all brick kilns in the state of Queretaro.

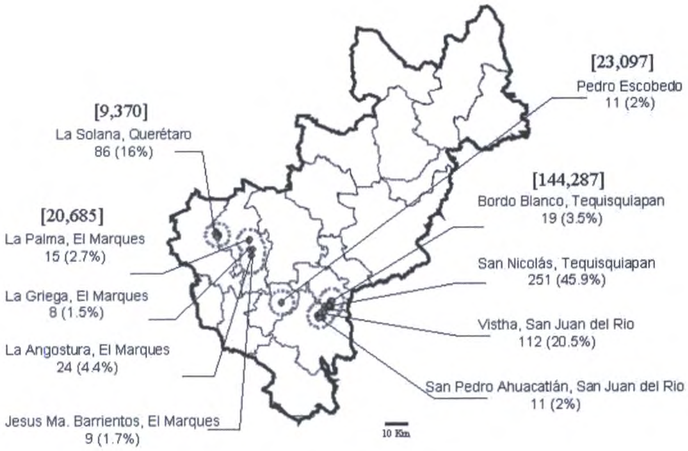

Figure 3. The location within the state of Queretaro of brick making kilns, along with the number and percentage of the total number of kilns, and the population living in a 5 km radius (dotted line).

Receptor co-location. Throughout the state of Queretaro, all brickmaking communities are located near or within centers of population, and along transportation corridors; 54.9 % and 45.1% of kilns are located within, and outside of, residential areas, respectively.

The potential for direct exposure and for dispersion by resuspension due to vehicular wake plumes is large. In and around the brickmaking communities of Queretaro state, approximately 197,500 persons are living within a radius of 5 km of a center of brick production (Table 2), approximately 144,300 in the San Juan del Rio-Tequisquiapan corridor. These local populations, including particularly the brickmaking personnel themselves, are likely to be exposed to toxic products of incomplete combustion, over prolonged periods of time.

There is an area of approximately 48,000 ha within a radius of 5 km of centers of brick production in the state (Table 2). Fifty percent of that area is used for irrigated agriculture, 33% for rain feed agriculture, and 3.8% for cultivated pasture. The rest (13%) is shrubland where animals roam freely. People, crops and domesticated animals constitute receptors of the emissions of brick kilns

Table 2. Receptors located within the 5 km estimated zone of influence of kilns in the state of Querétaro.

Receptor	Magnitude
Population (total)	197,500 persons
Land area (total)	48,339 ha
Irrigated agriculture	24,127 ha
Rain feed agriculture	16,057 ha
Crasicaul shrubland	5,596 ha
Subtropical shrubland	712 ha
Cultivated pasture	1,848 ha

Fuel inventory. The type of fuel used in the kilns varies seasonally, and according to the market. The fuel is generally a mix of available materials. Our survey results indicated (at one point in time) that 65 % of brickmakers self describe their fuel as fuel oil (n=194), 10.8% as recycled oil, 5.5% as a combination of fuel oil and wood, and 9.8% as other fuel (Table 3). There is evidence that in some cases these other fuels include hazardous waste. The fuel mix is tending toward fuel oil (combustoleo) but still consists in many cases of whatever material, waste, or recycled product is available (Table 1). Large amounts of fuel are used in the artisanal manufacture of bricks. Although the amount varies depending on the type of fuel used, an average 1400 L of fuel oil is employed to manufacture 10,000 bricks. These large amounts are partly due to the inefficiency of the baking process.

Table 3. Resource utilization for manufacture of 10,000 bricks and self reported usage of fuels in the state of Querétaro.

Raw materials	N	Amount	Self-reported usage
Fuels			
Fuel Oil/Recycled Oil	6	1546 ± 413 L	6 (2%)
Recycled Oil	16	1304 ± 288 L	32 (10.8%)
Fuel Oil	31	1403 ± 313 L	194 (65%)
Recycled Oil / Wood	6	407 ± 159 / 2 ± 0.38 ton	17 (5.8%)
Wood	1	3 ton ± 0	17 (5.5%)
Other/ Unknown	--	Unknown	29 (9.8)
Constituents			
Clay plus sand	12	49 m^3 ± 0.9	
Water	4	~10,000 L	

San Nicolas, Tequisquiapan

At a finer scale we have characterized the small community of San Nicolas, Tequisquiapan, which exhibits a particularly dense and co-mingled distribution of kilns, crops and human dwellings. Here we have conducted a finer-grained spatial analysis, including zones of influence of individual sources, fuel inventories, crop speciation, and population densities within these zones, along with basic micrometeorological information to determine likely emissions transport and deposition patterns. In this community we have also obtained photographic evidence of the density of plumes.

In the case of San Nicolás, a community of 4,147 residents in an area of 283 km^2, most of the kilns are located within the domestic compounds of family residential complexes, within the heart of the community (Fig. 1A, 4).

The annual mean wind is predominately from the NE (Fig. 4). The seasonal variation in speed and direction are currently under evaluation.

Emissions

We have obtained samples of airborne and soil-deposited particles for gravimetric and chemical characterization (not shown), documenting elevated levels of polychlorinated biphenyls (PCB) in the ashes recovered from kilns in San Nicolas (Gómez et al. unpublished). The presence of polycyclic aromatic hydrocarbons (PAH) and chlorinated aromatic hydrocarbons (CAH), including dioxins and furans, is likely, given the types of products employed as fuel.

The persistence of CAHs in the environment and in organisms, their bioaccumulation through the food chain, and their toxicity depend on the specific chemical composition, particularly the number and position of chlorine atoms in the molecules (Geyer et al. 2002). The most biologically active, and thus toxic, CAHs are the planar molecules with chlorine in the four lateral positions. For example, 2,3,7,8-tetraclorodibenzo-p-dioxin (TCDD) is the most toxic of the common CAHs.

In contrast to the PCBs, that were intentionally manufactured over a period of many years for industrial applications, dioxins and furans were not produced intentionally and are undesirable byproducts of bleaching in the paper industry, production of certain pesticides, and of a variety of incineration processes of municipal, hospital and toxic wastes (Fiedler 1996; Dyke et al. 1997). Their presence near fuel oil respositories in brickmaking communities suggests that they may be contaminants of the fuel itself, whereas their presence only in ash or aerial emissions could be equivocal, suggesting a possible byproduct of partial combustion during the brickmaking process itself.

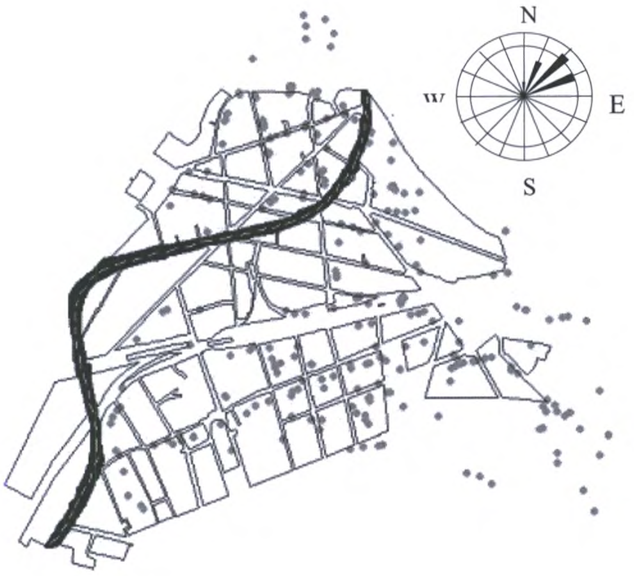

Figure 4. Map of the community of San Nicolás, Tequisquiapan, Qro. The points indicate the location of individual brick kilns. The dark line indicates Mexico Highway 120, a major intercity transporatation corridor. The annual mean wind is predominately from the northeast.

The furans and PCBs exhibit physical and chemical properties, and environmental fates, similar to the dioxins, and are equally recalcitrant in the environment and similarly lipophilic. PCBs represent a family of 209 chlorinated compounds produced either intentionally or inadvertently, with no known source in the natural environment. A prominent former use of PCBs, due to their great stability and inertness, was in transformers and other electrical devices. Their environmental stability and toxicity led to their discontinued use, and to the generation of an illicit supply of waste transformer oil contaminated with PCBs. The CAHs also bioaccumulate and biomagnify, and exhibit considerable persistence in the environment.

Biological Effects

We have determined biological impacts of emissions on non-domesticated target mammals trapped in the wild (field mice: *Myotis spp*). We evaluated the frequency of micronuclei in peripheral erythrocytes and determined DNA breaks on peripheral lymphocytes assessed using the alkaline comet assay (Fig. 5). These assays are widely used to assess genetic damage *in vivo* and *in vitro* (Moller et al., 2000, Martin et al. 2005, Pitarque et al. 2002). Wild indigenous mice captured from San Nicolas (n=35) exhibited, on average, a seven-fold higher frequency of micronuclei than the control (n=10) group ($P<0.05$; Fig. 5A). Similarly, 39.8% of cells of exposed animals (n=20) exhibited abnormal (tail > 10% of head) comets, as opposed to only 14.6% in the control (n=9) group. Furthermore, the average comet tail length for the exposed group averaged 8.3 µm, 1.7-fold longer than for the control ($P<0.05$; Fig. 5B). These results suggest the presence of mutagenic compounds in the emissions of brick kilns.

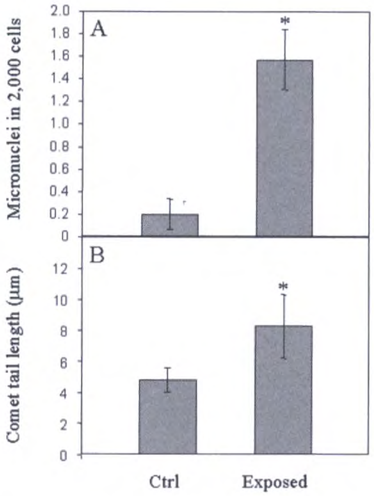

Figure 5. Biological effects. A) Micronuclei in peripheral red blood cells and B) Length of abnormal comet tails indicating DNA breaks in peripheral lymphocytes assessed by the alkaline comet assay.

Many of the compounds that are expected to be present in emissions from the brick ovens are powerful air toxics, causing considerable biological damage to organisms. Once HAHs are taken up by organisms, due to their low rates of metabolism, biodegradation and elimination, and high lipophilicity, the exposure to these compounds is cumulative, leading to persistent internal exposure from adipose tissue. It is estimated that the residence time (half-life of TCDD) in humans is approximately 8 years (Geyer et al. 2002).

Exposure to TCDD, for example, produces diverse effects including tumor generation and cancers, teratogenic effects, immunosuppression, atrophy of the thymus gland, hepatotoxicity, dermatological toxicity, endocrine disruption as well as reproductive disruption and death. (Safe 1993; Safe 1995; Denison and Heath-Pagliuso 1998; Bertazzi et al. 2001; Kerkvliet 2002).

Accidental exposure of humans to PCBs, and experimental studies with animals, demonstrate dermatological responses (chloracne), as well as immunosuppression, behavioral changes, and reproductive anomalies associated with endocrine disruption (Faqi et al. 1998; ATSDR 2000). Human exposure *in utero* has been demonstrated to cause negative effects in adulthood on production and vigor of sperm (Guo et al. 2000).

Future Plans

The deposition of particles to plant leaves and surrogate surfaces, their composition, and biological impacts on plants will be undertaken in the vicinity of the kilns. These data will extend the evidence of mammalian health hazards, to other components of the environment, and will investigate risks to the food chain.

Particles of kiln ash, and soil near these passive monitors will be collected as well. Suspended particles will be collected using polycarbonate Petri dishes and exposed horizontally for two weeks at 1 m above the ground, according to the method of Bytnerowicz et al. (1987) Leaves of tree species, and of marketable commodities (particularly ripening *Sorghum* heads, if available), will be collected nearby, according to the method of Freer-Smith et al. (1997). Petri dishes will be located in pairs. Half of the leaves and one of the petri dishes will be washed with dH_2O and the rinsate filtered for gravimetric determination of particulate load. The other half will be washed 3x in dichloromethane for characterization of surface deposited particles, followed by complete extraction of the leaves in dichloromethane to determine uptake into the tissues.

Effects on vegetation will be analyzed by evaluation of genotoxicity using Tradescantia pollen tetrads (Ma et al. 1994) and a pollen viability assay of plants growing in the vicinity of kilns (Micieta and Murin; 1996).