



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 (NH₃), hydrogen sulfide (H₂S), carbon dioxide (CO₂) and particulate matter (including total suspended particulate (TSP) and PM₁₀) 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 NH₃, H₂S, and CO₂, continuous for PM₁₀, 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 H₂S concentrations were similar in both types of barns, varying from 0.4 to 0.6 ppm. NH₃ emissions from the deep pit finishing barns were also higher (50 to 60 g NH₃/d-AU) than from the pull plug building (35 to 40 g NH₃/d-AU) but H₂S emissions were somewhat similar, 3.0 to 4.0 and 4.0 to 4.5 g H₂S/d-AU for the pull-plug and deep-pit barns respectively. The pull plug finishing barns experienced higher PM₁₀ concentrations (450 to 500 vs. 150 to 170 μ g PM₁₀/m³) and emissions (3.0 vs. 0.75 g PM₁₀/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/m³) 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

PM₁₀ – two “tapered element oscillating microbalances” or TEOM ambient PM₁₀ 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. PM₁₀ 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 m³/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:

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

where:

E = Barn emission rate, mg/s or µg/s

Q_o' = Dry standard ventilation rate at barn exhaust (based on STP), dsm³/s

C_o' = Standardized mass concentration at the barn exhaust (based on STP), mg/dsm³ or µg/dsm³

Q_i' = Dry standard ventilation rate at the barn inlet (based on STP), dsm³/s

C_i' = Standardized mass concentration at the barn air inlet (based on STP), mg/dsm³ or µg/dsm³

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.

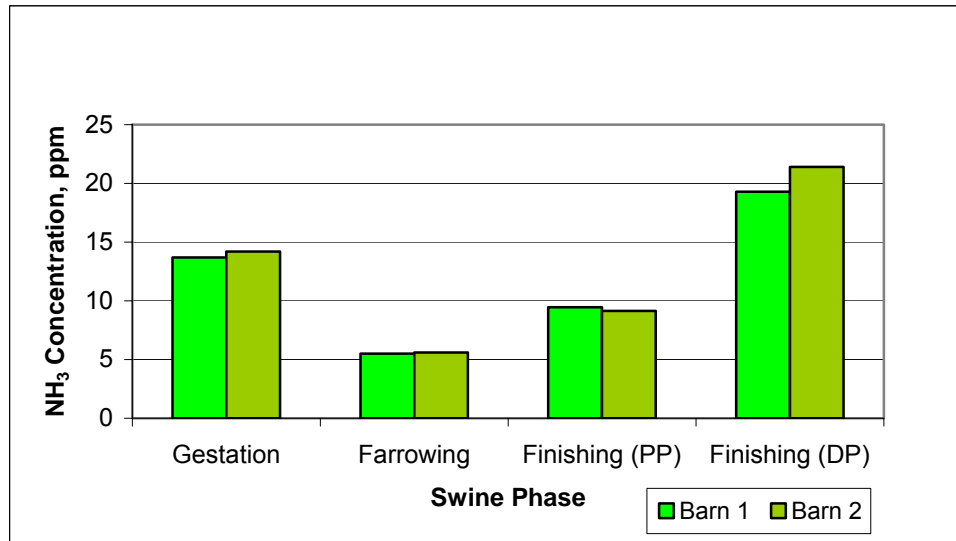


Figure 1. Average Ammonia Concentrations

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 \pm 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 $13.6 \pm 9.4^\circ\text{C}$ whereas the Iowa site's mean temperature was $7.0 \pm 11.9^\circ\text{C}$ 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.

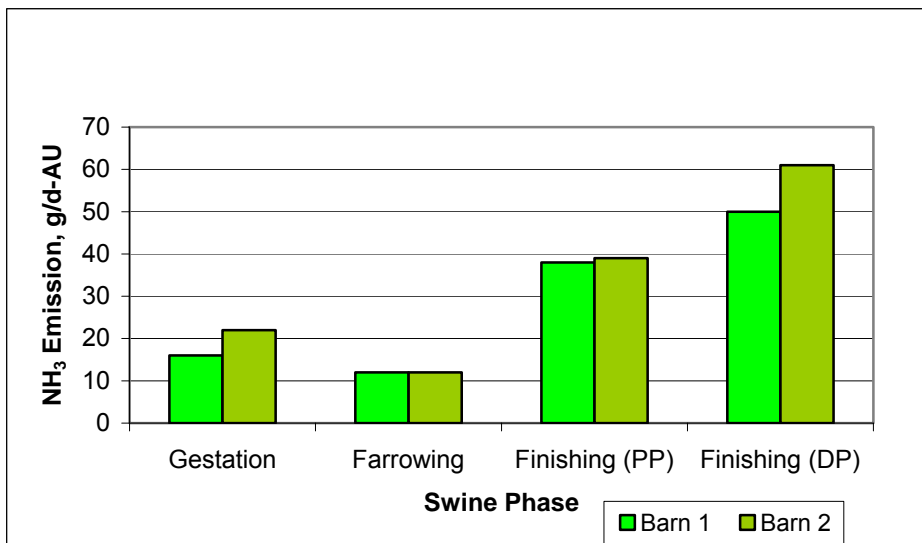


Figure 2. Average Ammonia Emissions

The hydrogen sulfide concentration results again were lowest for the Illinois farrowing rooms with an average H₂S concentration of only 292±148 ppb as shown in figure 3. The H₂S 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 H₂S concentration of 591±185 ppb. The PP finishing site had a H₂S concentration of 588±611 ppb and the DP finishing site had a H₂S concentration of 434±234 ppb. Figure 4 represents the H₂S 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 H₂S 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 H₂S emission rate of 4.3±2.8 and 3.4±3.0 g/d-AU for the PP and DP sites, respectively.

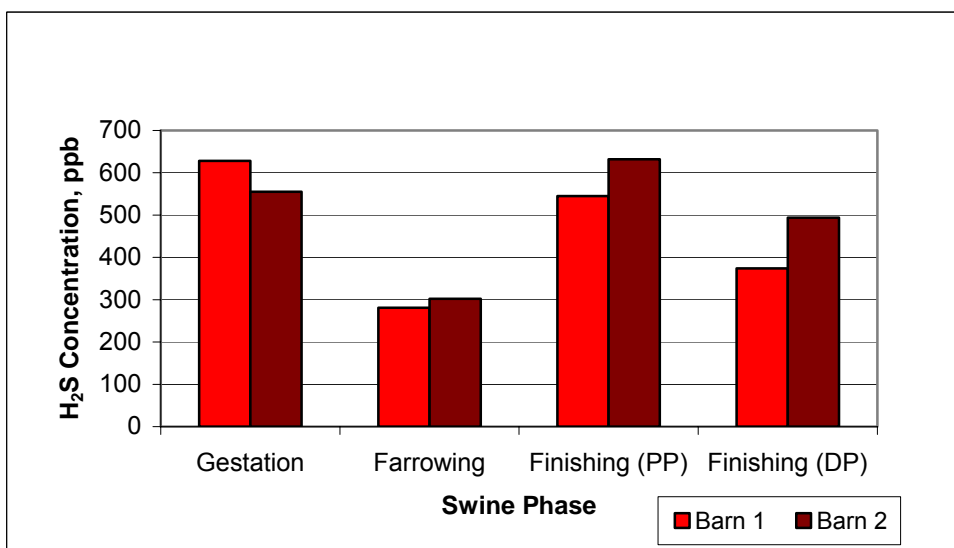


Figure 3. Average Hydrogen Sulfide Concentrations

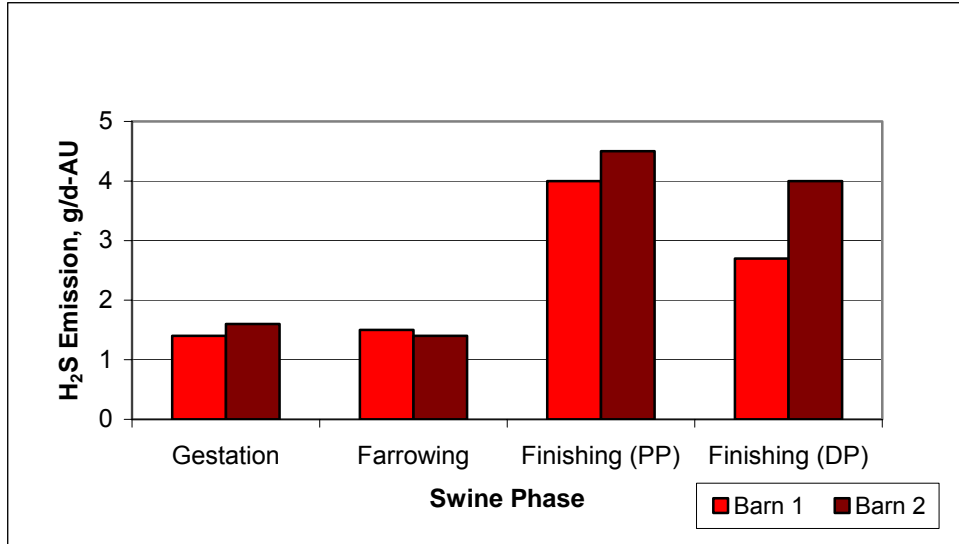


Figure 4. Average Hydrogen Sulfide Emissions

The results of the PM₁₀ measurements for these four sites are shown in figures 5 and 6. The Iowa DP finishing barns were the lowest in both PM₁₀ concentrations and emissions with averages of 158±102 □g/m³ and 0.8±0.6 g/d-AU respectively. The Texas PP finishing barns had a higher average PM₁₀ concentration (467±238 □g/m³) and greater PM₁₀ 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.

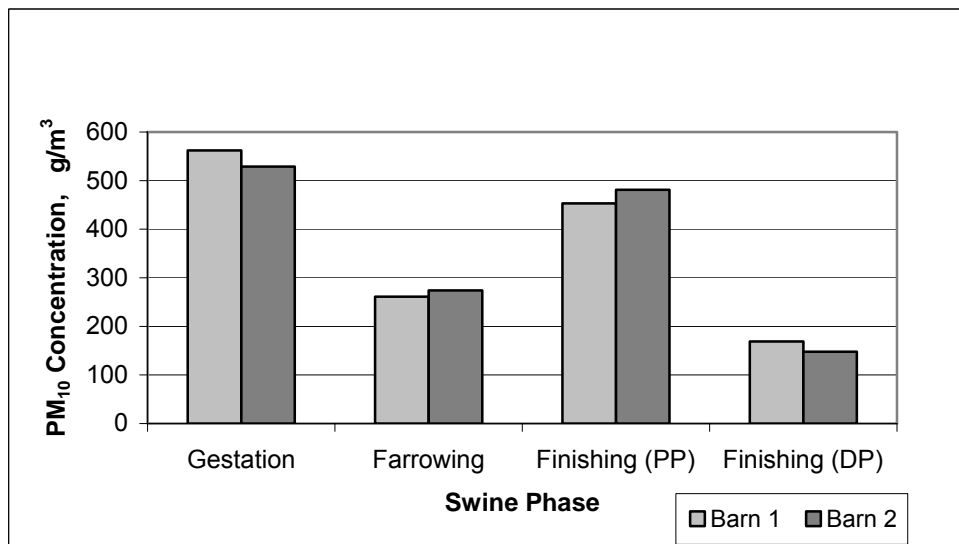


Figure 5. Average PM₁₀ Concentrations

The gestation barns had the highest average PM₁₀ concentration of 545±240 □g/m³ 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 PM₁₀ concentrations during filling and sow feeding events. The farrowing rooms had an average PM₁₀ concentration of 267±179 mg/m³ with an average emission of 1.2±1.1 g/d-AU.

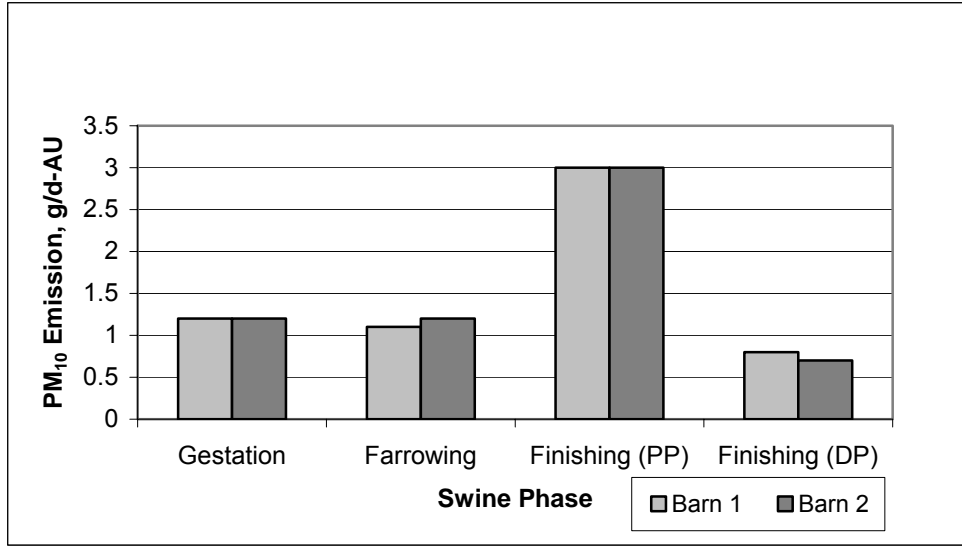


Figure 6. Average PM₁₀ Emissions

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/m³ 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/m³, 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/m³ and 43±29 OU/s-AU, respectively. The gestation barns had an average concentration of 970±630 OU/m³ 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.

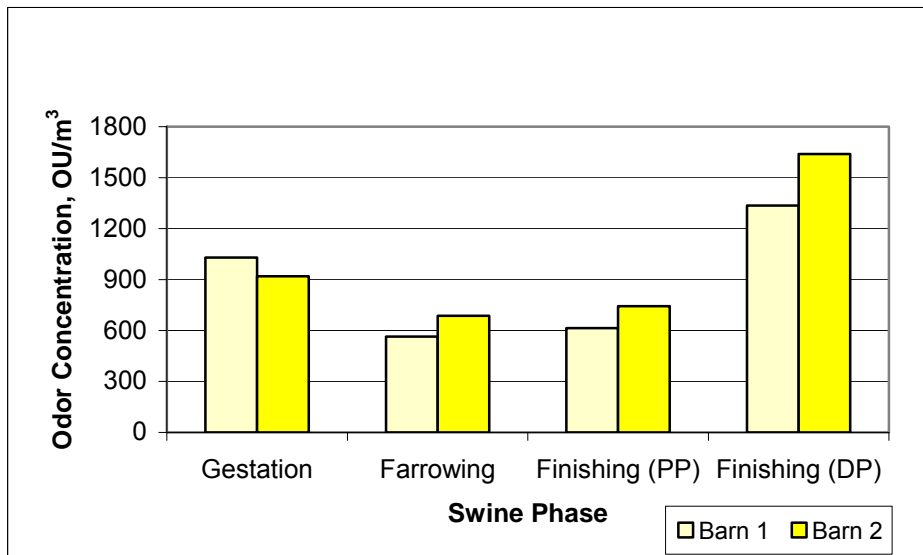


Figure 7. Average Odor Concentrations

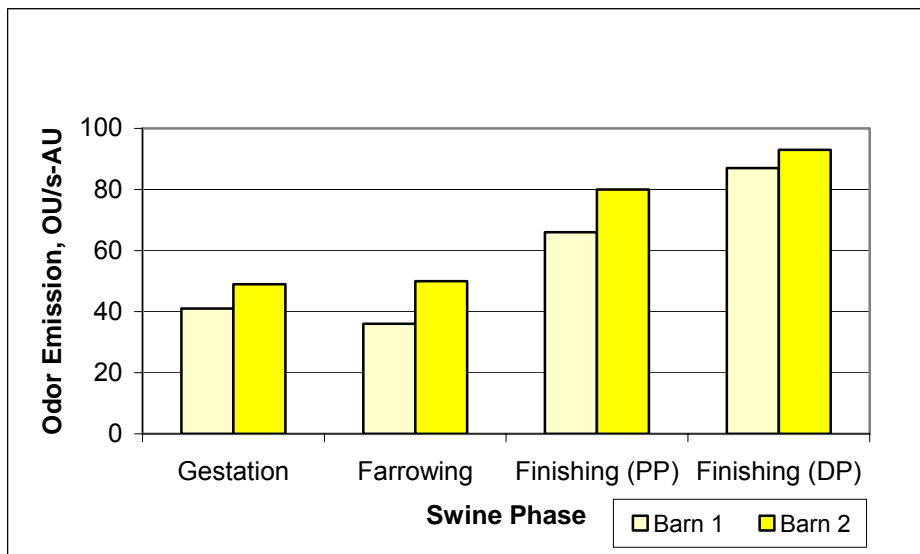


Figure 8. Average Odor Emissions

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 NH₃ and H₂S of 45 kg/d under CERCLA and EPCRA, since theoretically only a single day’s emissions would be required. In general, NH₃ 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 NH₃, H₂S, and odor. The PM₁₀ 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 NH₃ and H₂S.

Daily Max	NH ₃ , ppm		NH ₃ , g/d-AU		H ₂ S, ppm		H ₂ S, 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 PM₁₀ and Odor.

Daily Max	PM ₁₀ , g/m ³		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 H₂S concentrations were similar in both types of barns, varying from 0.4 to 0.6 ppm. NH₃ emissions from the deep pit finishing barns were also higher (50 to 60 g NH₃/d-AU) than from the pull plug building (35 to 40 g NH₃/d-AU) but H₂S emissions were somewhat similar, 3.0 to 4.0 and 4.0 to 4.5 g H₂S/d-AU for the pull-plug and deep-pit barns respectively. The pull plug finishing barns experienced higher PM₁₀ concentrations (450 to 500 vs. 150 to 170 μ g PM₁₀/m³) and emissions (3.0 vs 0.75 g PM₁₀/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/m³) 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.

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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 (NH₃), 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 NH₃ 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 NH₃ emissions (30GgNH₃/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 NH₃ 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.

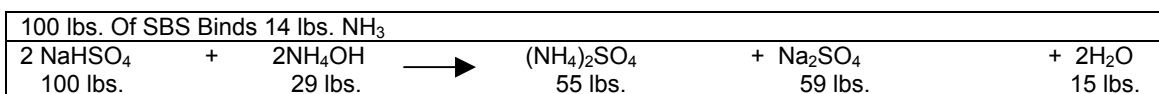


Figure 1. Binding of Ammonia by SBS to produce Ammonium Sulfate

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 SO₄⁼ 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 NH₃ 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/9.29m² 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 NH₃ 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.

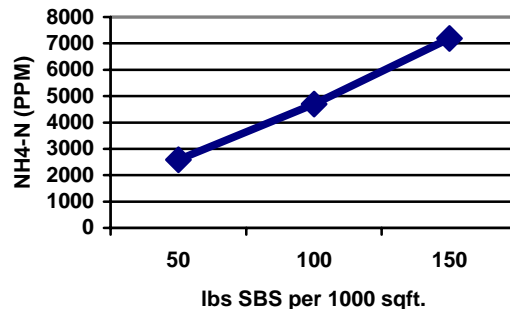
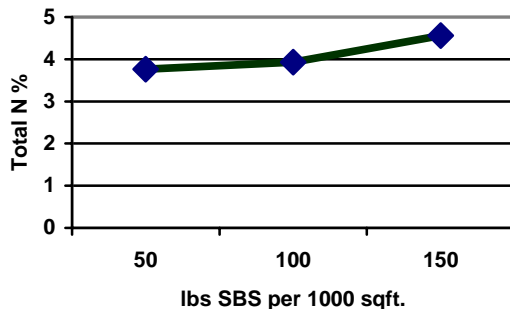
		Pre-Treatment	Post-Treatment	Time (weeks)						
				1	2	3	4	5	6	7
Ammonia (PPM)	Treated	127	0	0	5	8	15	19	20	18
	Control	119	119	125	125	138	114	128	98	97
Litter pH	Treated	8.5	1.7	2.1	3.4	4.5	5.0	5.5	5.9	6.4
	Control	8.9	8.9	8.7	9.1	8.5	9.3	8.6	8.1	8.9

Current SBS Research in Poultry

A two-year NH₃ 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 NH₃ 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 NH₄-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/m² or 1.95 kg/m² 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/cm²/min). As in the UGA study, manure ammonium (NH₄⁺) nitrogen and P₂O₅ were positively altered by treatment group with the high-rate treatment group having the highest level of retained nitrogen and the lowest level of P₂O₅ (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 ₂ O 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/9.29m² (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 outperformed 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 (Agrimetrix 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 NH₃ 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/m² and all treated samples at 0 Flux (mg/hr/m²).

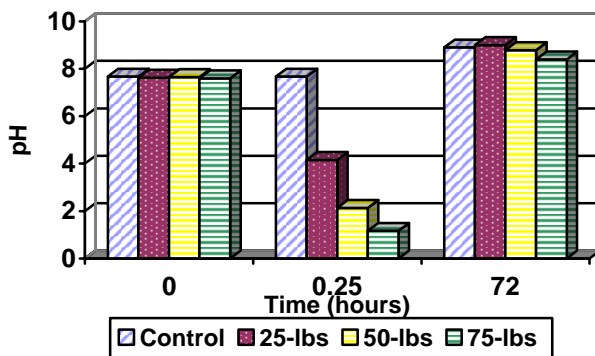


Figure 4. pH readings of dairy slurry treated with SBS (lbs/1000 sqft) over time.

Ammonia flux increased as time increased but there was always a linear decrease in NH₃ flux as treatment rate increased (Fig. 5-7). Most interestingly, NH₃ 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.

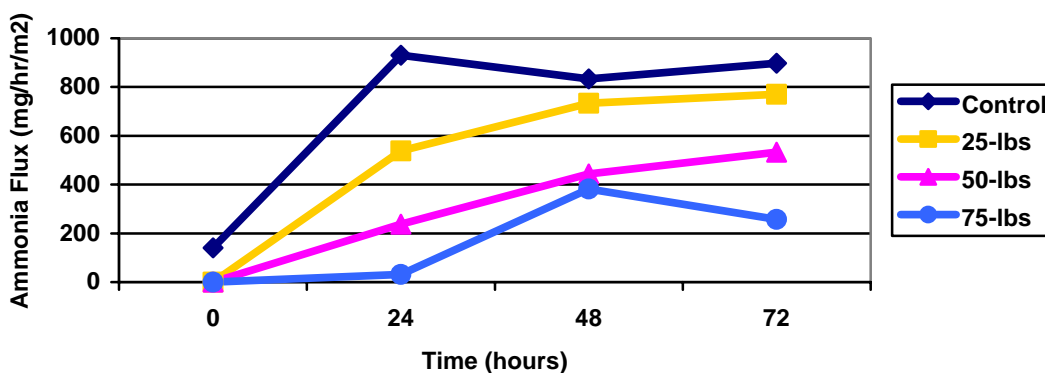


Figure 5. Week 1 Ammonia Flux (mg/hr/m²) of dairy slurry treated with SBS (lbs/1000 sqft).

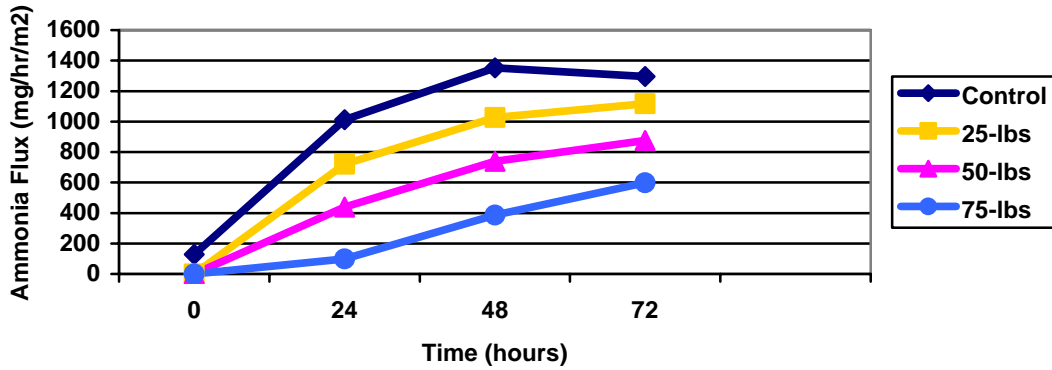


Figure 6. Week 2 Ammonia Flux (mg/hr/m²) of dairy slurry treated with SBS (lbs/1000 sqft).

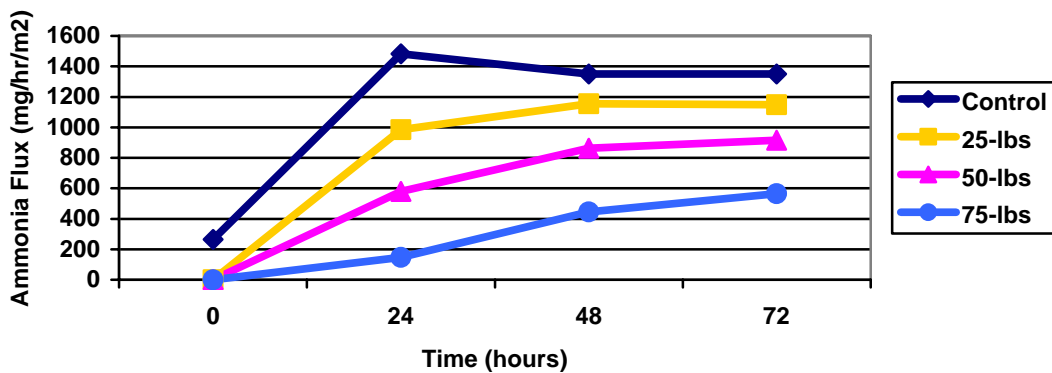


Figure 7. Week 3 Ammonia Flux (mg/hr/m²) of dairy slurry treated with SBS (lbs/1000 sqft).

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) PM_{2.5} data was used in addition to IMPROVE aerosol data. Surface PM_{2.5} 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 $97 \times 97 \times 32$, $154 \times 154 \times 32$, and $27 \times 27 \times 32$ 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.

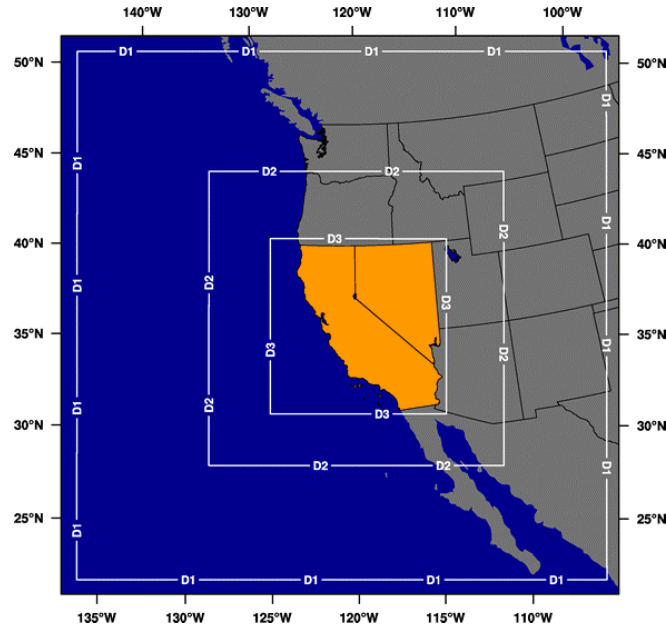


Figure 1. Three-nested domain of CANSAC MM5 forecasts. D1, D2, and D3 represent the borders of 36 km, 12 km, and 4 km grids, respectively.

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.

Burning Index

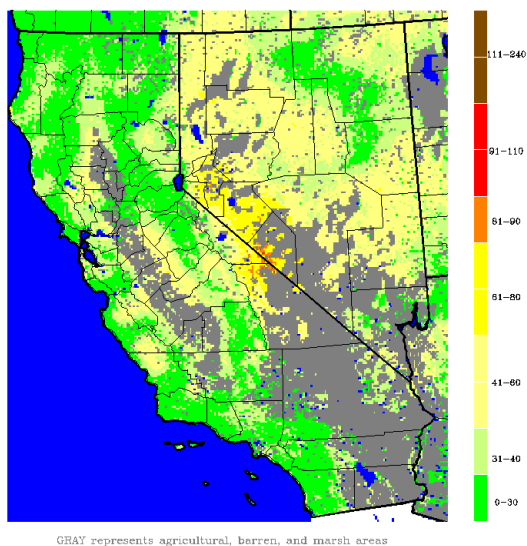


Figure 2. Gridded burning index map calculated for the CANSAC 4 km California and Nevada domain.

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).

Prescribed Fire & Wildfire Simulation

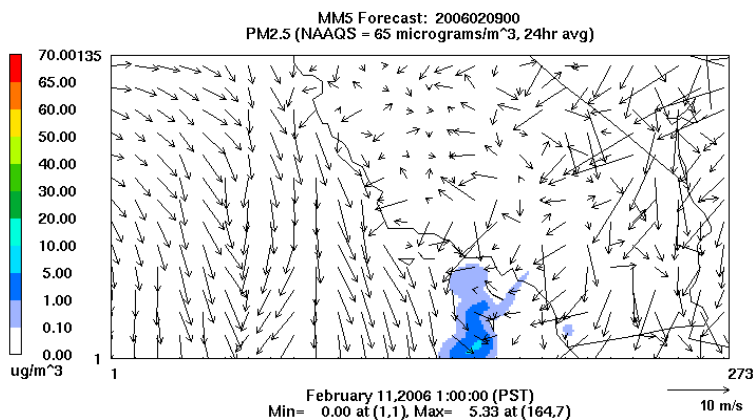


Figure 3. BlueSky PM_{2.5} concentrations from a wildfire in southern California, 11 February 2006.

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 OCIO 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

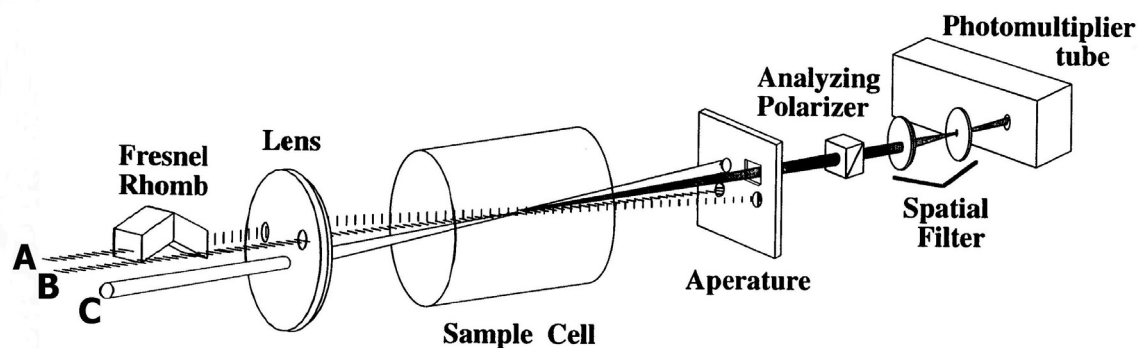
Photodissociation studies of small polyatomic molecules have opened the way to understanding two important aspects of reaction dynamics: selective bond fission and the breakdown of the Born-Oppenheimer approximation. The relationship between these two phenomena has manifested itself in studies of reaction 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 coworkers³ 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 OCIO following near-UV excitation is one of those few examples.

The absorption spectrum of OCIO 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 OCIO 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 OCIO levels having *asymmetric stretching* ($\nu_1-1, 0, 2$) character.

Competitive dissociation pathways in the photolysis of OCIO 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 ($\lambda < 400$ nm), OCIO 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 Werner⁸ indicate that another dark state, the strongly-bent 2B_2 state, exhibits two transition states to dissociation. On the 2B_2 potential surface, Cl + O₂ 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 OCIO.

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 OCIO molecules populate vibrationally excited states and this contribution is neglected in current models. Transitions involving a vibrating OCIO 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 OCIO. 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 OCIO. 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) →

($v_1,0,0$). This enhancement is less prominent for transitions to bending combination bands ($v_1,1,0$) and asymmetric stretching combinations ($v_1,0,2$); and least noticeable for transitions to a mixed combination band ($v_1,1,2$).

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 study⁹ of the low-lying excited states of OBrO indicate that a branching between $\text{BrO} + \text{O}$ and $\text{Br} + \text{O}_2$ 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/km². 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 as 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.al., 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 al., 2002b). It is necessary also to develop new approaches in crops nutrition and agricultural wastes management to increase degraded soil biological activity.

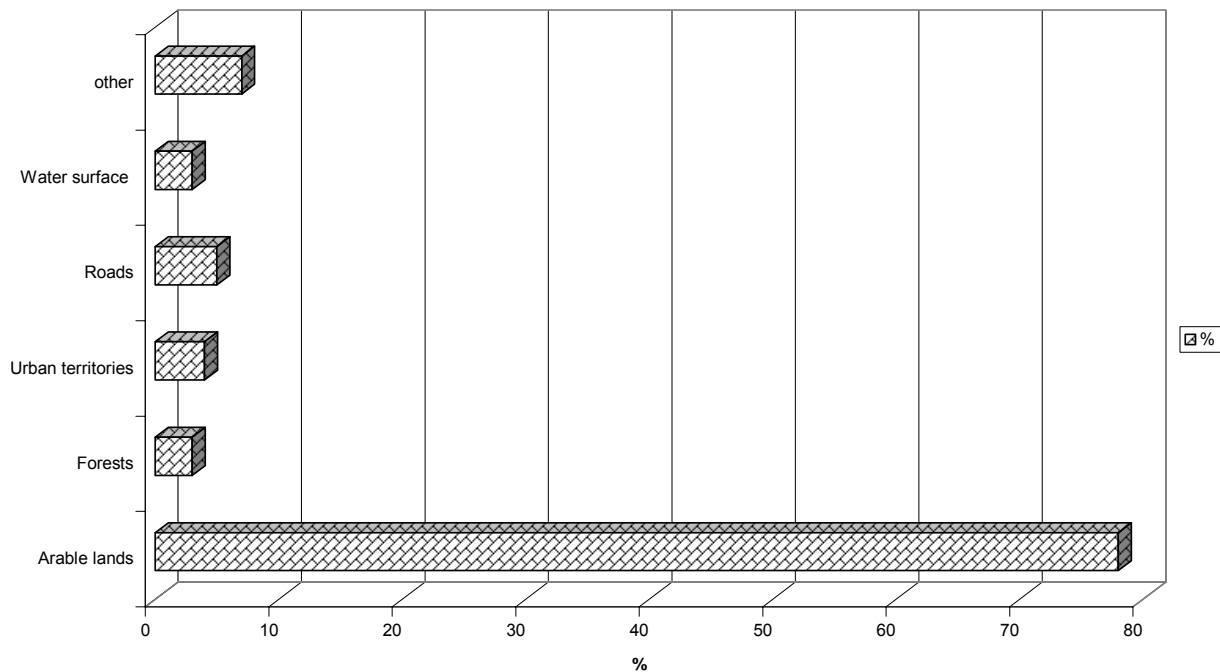
Methods

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 Dniپر 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 al., 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 mollisol. 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/km². 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 al., 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 $\mu\text{g}/\text{m}^3$ respectively. PM_{10} concentration is about three times higher than the national standard value of 60 $\mu\text{g}/\text{m}^3$. 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

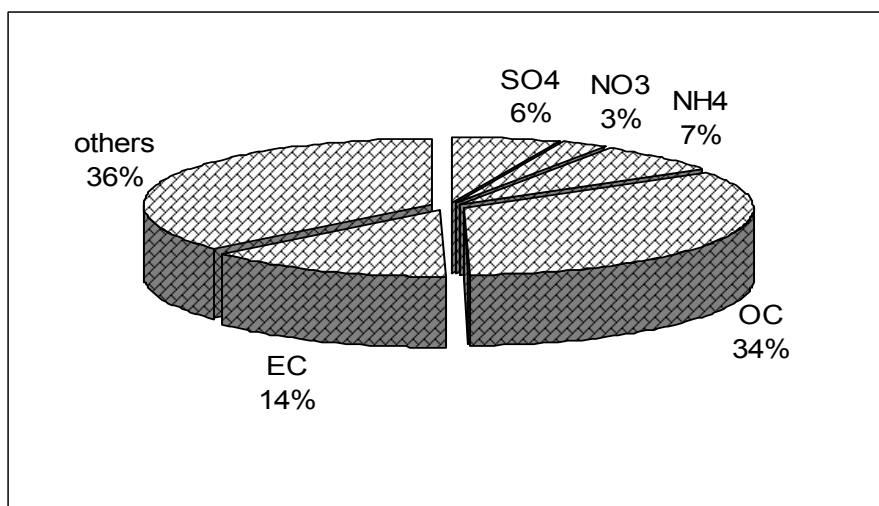


Figure 1. Percentage of analysed species in PM10 at Natthupura

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.

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Measurements of N₂O Emissions from Agricultural Soil in Southwestern Korea

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Abstract

A closed flux chamber system was used for measuring nitrous oxide (N₂O) 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, N₂O 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. Based on agricultural soil emission data, monthly averaged N₂O fluxes during May, June, and July were 0.14±0.08, 0.05±0.03, and 0.13±0.06 mg-N₂O m⁻²h⁻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 N₂O flux and soil moisture. Soil N₂O 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 N₂O emission should be not neglected in estimation estimating the national emission inventory.

Introduction

In the lower atmosphere, total oxides of nitrogen (NO_x) 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 (N₂O) 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 N₂O is about 250 times greater than each molecule of CO₂. N₂O 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 N₂O, contributing about 57% (9 Tg y⁻¹) of the total annual global emission. Mosier et al. (1998) reported that most atmospheric N₂O is of biogenic origin and produced by bacteria in soils. N₂O 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 N₂O 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 N₂O 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 N₂O, 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).

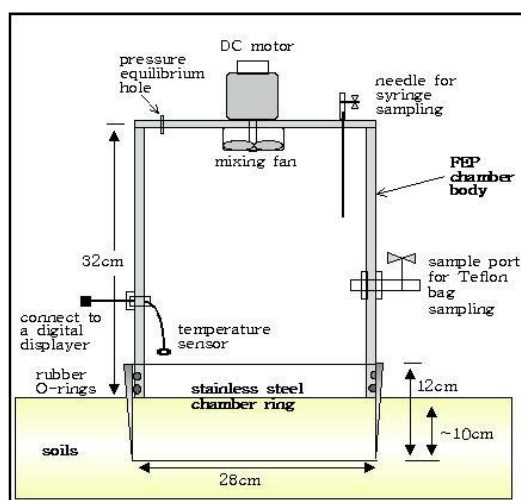
The southwestern coastal plain in Korea is the most intensively cultivated area. Rice cultivating area in the plain accounts for ~34% of the total cultivated area in Korea and contributes ~35% of the total annual national rice production. Agricultural activities in this area have been intensifying over 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 m²; 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).

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

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 $0.10 \pm 0.07 \text{ mg-N}_2\text{O m}^{-2} \text{ h}^{-1}$ over the period. The N_2O emissions range from 0.01 to $0.25 \text{ mg-N}_2\text{O m}^{-2} \text{ h}^{-1}$. On monthly base, minimum average N_2O emission, $0.05 \pm 0.03 \text{ mg-N}_2\text{O m}^{-2} \text{ h}^{-1}$, was recorded in June and maximum in May was $0.14 \pm 0.08 \text{ mg-N}_2\text{O m}^{-2} \text{ h}^{-1}$ 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- $\text{N}_2\text{O}/$ m^2/hr	WFPS (%)	Soil Temp ($^{\circ}\text{C}$)	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).

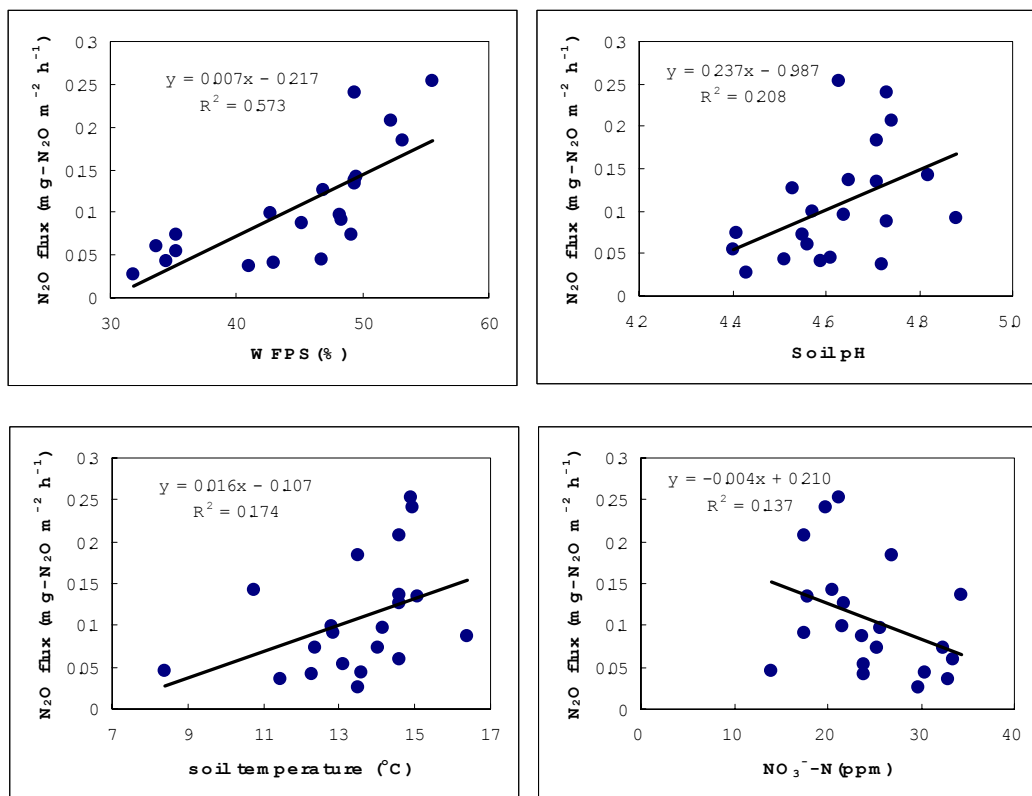


Figure 2. Relationship between soil N₂O flux and soil parameters during the experimental period

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 N₂O 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 N₂O flux and soil moisture. Soil N₂O emissions from rice paddy were significantly lower than those from upland soils; anoxic condition due to flooded water could restrict surface release of N₂O by producing nitrate reduction. It could suggest that contribution from agricultural soil to the national N₂O emission would be important. Even from the flooded paddy field, there was sufficient N₂O emission was detected. N₂O 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 NH_4^+ 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 ($= \text{NH}_3 + \text{NH}_4^+$) 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 their 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 NADP 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 effort 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 puffs 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 multiplied 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 performed 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 NH_4 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

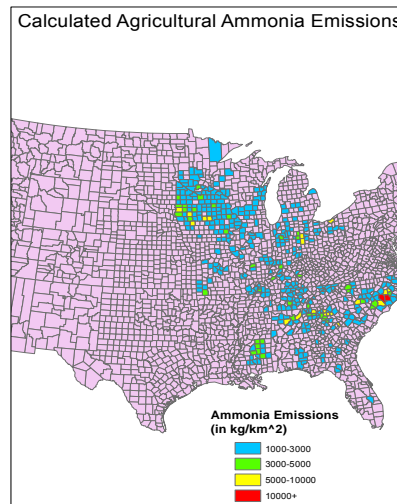


Figure 1. Spatial distribution of NH₃ emissions (kg/sq. mile/ year).

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 NH₃ 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

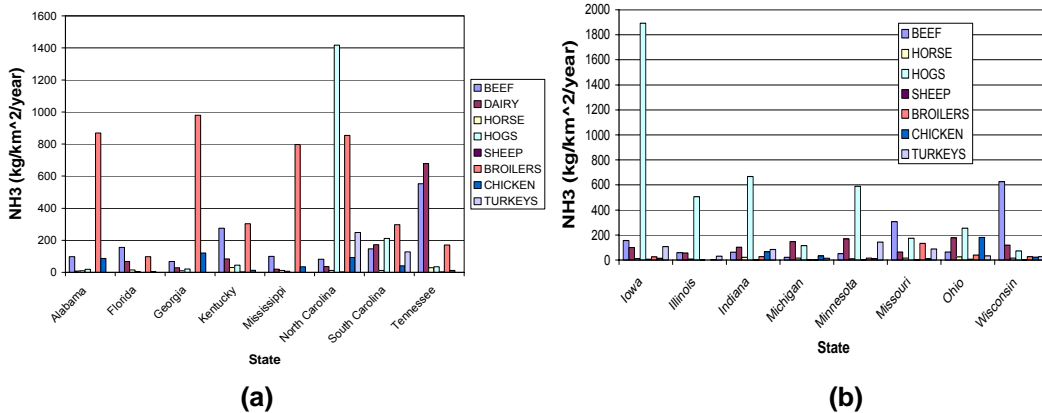


Figure 2. Total ammonia emissions from specific agricultural sources, by state, in the Southeast (a) and Midwest (b) United States.

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 NH₃ 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.

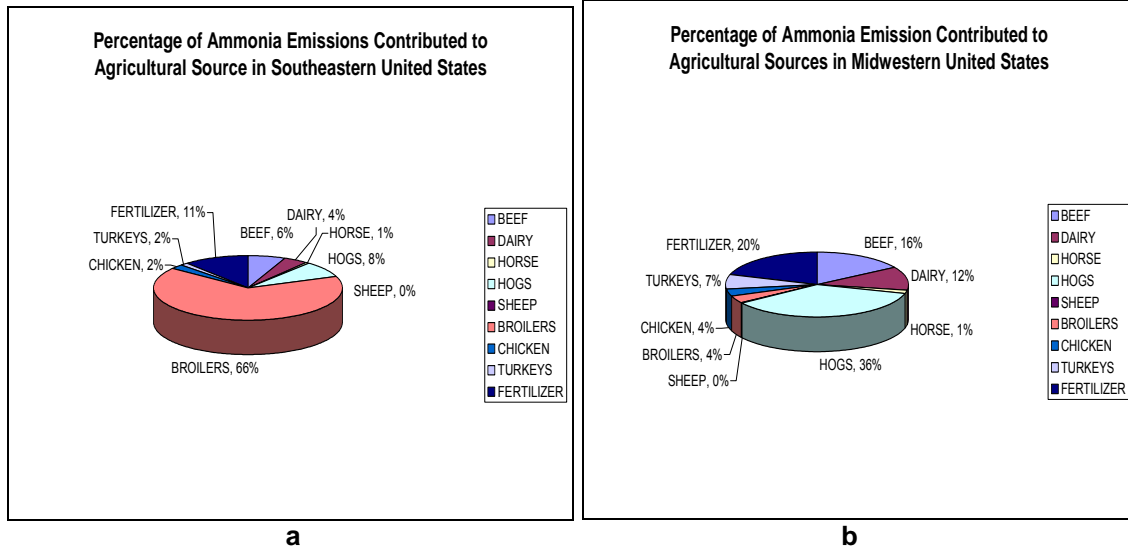


Figure 3. Emissions from specific agricultural sources, by region [Southeast (a) and Midwest (b) United States]

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 that livestock 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.

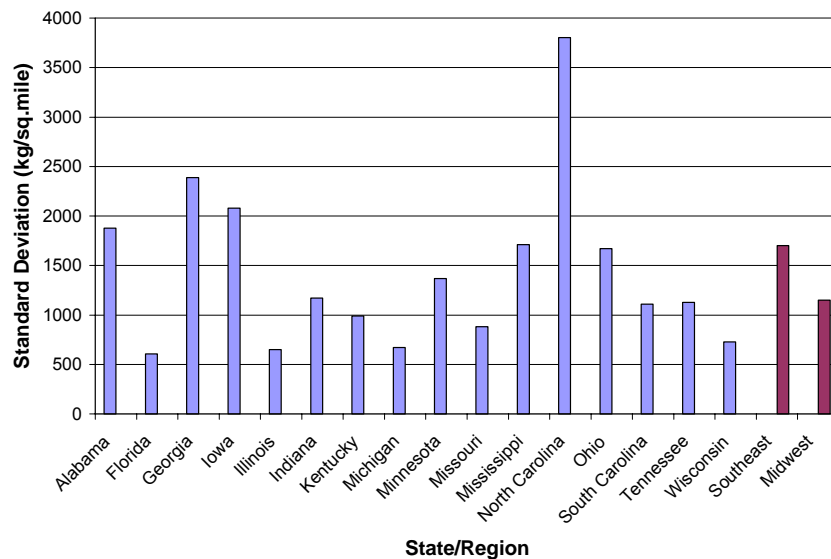


Figure 4. Standard deviation of ammonia emissions between counties in specific states.

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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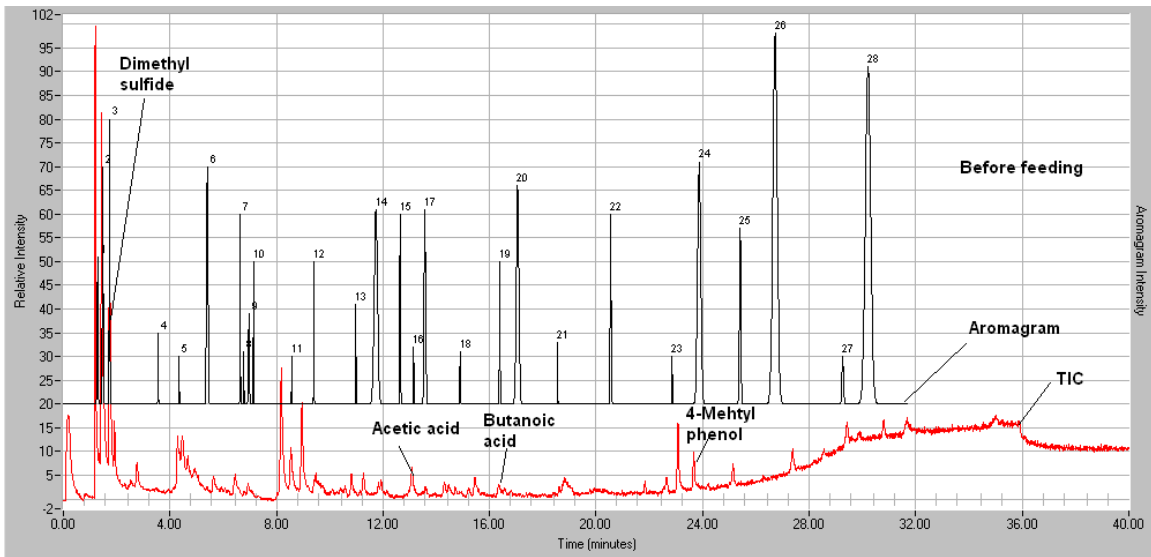
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Abstract

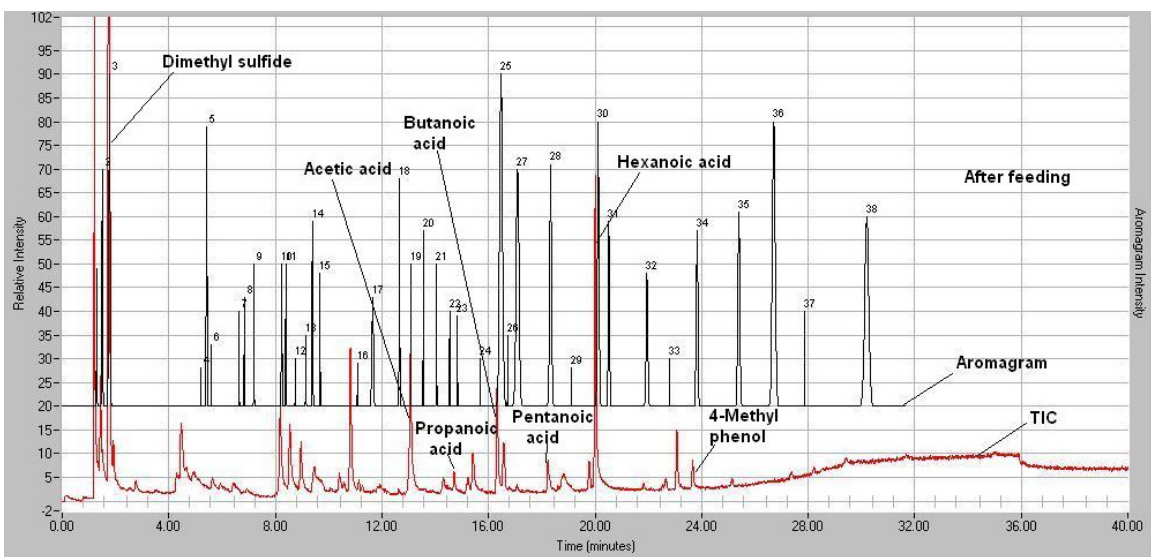
Cattle production is associated with aerial emissions of odor, volatile organic compounds (VOCs) and other gases originating mainly from manure and the animal itself. Chemical composition of rumen liquid and gas can affect aerial emissions. Rumen headspace is saturated with compounds produced during 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 μ m 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 μ m 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 et 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 multidimensional 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-aminoacetophenone = 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 emissions 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.

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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 emission 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 effectiveness 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 $64.8 \text{ kg} \pm 5.4 \text{ SD}$) 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 be 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 \pm 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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