



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

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### **Introduction**

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

### **Materials and Methods**

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

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

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

Total and respirable gravimetric dust concentrations were determined using NIOSH Methods 0500 and 0600, respectively. Flow rates of the pumps were calibrated at 2 L/min for measuring total dust concentration and 1.7 L/min for respirable dust concentrations. Pump flow rates were calibrated with a rotameter prior to and at the end of each sampling event. Sampling time averaged approximately five hours during tunnel fan operation. Both blank and background samples were obtained for each sampling event. The pre-weighed cassettes were supplied and analyzed by a certified laboratory (Data Chem Laboratories,

Inc., Salt Lake City, UT). A Dust Trak Model 8520 (TSI Inc., St. Paul, MN) was used during 2004 as an additional procedure for total dust determination. These units provide the added advantage of getting real-time analysis during the 5-hour sampling events.

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

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

### Results and Discussion

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

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

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

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

## Conclusions

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

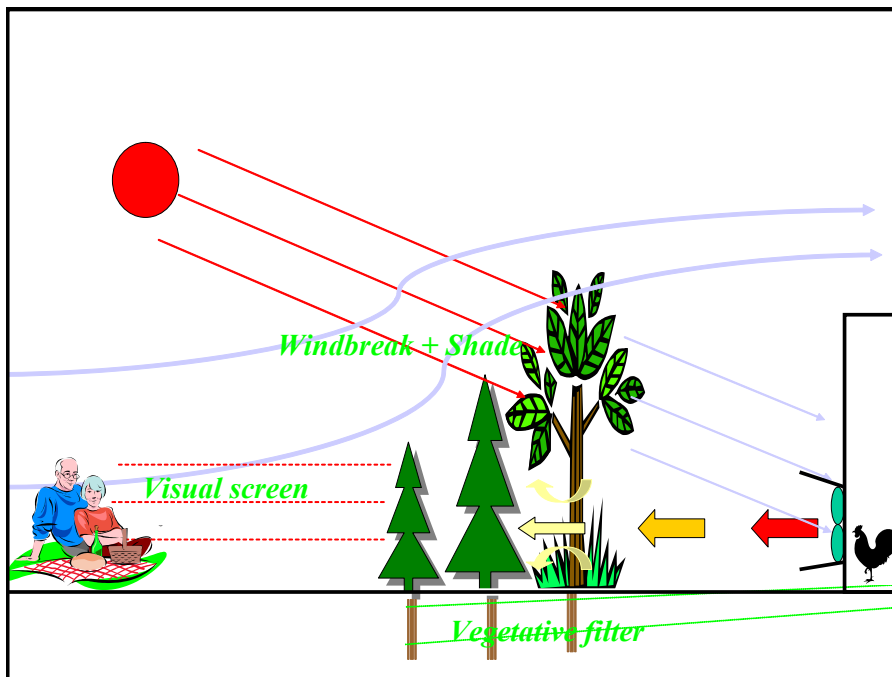


Figure 1. Goals of a vegetative environmental buffer.



**Figure 2. Planting arrangement of trees opposite tunnel fans.**



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



## **Establishment of Vegetative Environmental Buffers Around Poultry Farms**

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### **Introduction**

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

### **Lessons Learned From Vegetative Environmental Buffer Planting Demonstrations**

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

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

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

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the farm. To be responsive and proactive to escalating neighbor-relations and emission issues, the local poultry industry trade association plans to hire a coordinator to facilitate in the design, installation and maintenance of VEB on poultry farms in this area.

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

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### Introduction

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

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

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

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

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

### Methods

#### System

Using a unique mobile sampling methodology employing 21 foot helium balloons and a variety of air and climatic sampling equipment, trace gases (carbon dioxide, methane, nitrous oxide) and N gas and particle species (nitric acid, ammonia, ammonium) were measured at five heights at three locations downwind, and three heights at one location upwind of two dairies. In addition, detailed micrometeorological data were collected for each sample height including temperature, relative humidity, wind speed and direction. These data were used to characterize the dispersion and concentration of the emission plume coming from the

dairy. This innovative mass balance measurement technique was designed to overcome the limitations of other sampling systems and provide a spatially resolved characterization of the emission plume. For more detailed information about the measurement system, see accompanying conference paper entitled: **A** boundary layer sampling methodology for measuring gaseous emissions from CAFO's (Marcillac et al, 2006).

### Emission Sampling Scheme and Site Descriptions

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

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

## Results and Discussion

### Climatic Data

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

### Emissions data

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

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



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

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

<sup>a</sup>Morning is any sample time before 1100 h

<sup>b</sup>Afternoon is any sample time between 1100 - 1700 h

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

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

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

Measure	HNO <sub>3</sub> ppbv	NH <sub>3</sub> ppbv	NH <sub>4</sub> ppb(w/w)	CO <sub>2</sub> ppmv	CH <sub>4</sub> ppmv	N <sub>2</sub> O ppbv
<i>Global background<sup>a</sup></i>	NA	1-10	NA	370	1.72	320
Total upwind, avg	1.89	48.8	0.37	399	2.01	326
Total downwind, avg	1.64	236.1	0.45	406	2.34	328
<i>Seasonal downwind, avg</i>						
Summer	1.00	299.5	0.36	420	2.49	329
Fall	2.93	109.3	0.63	396	2.13	326
Winter	-	-	-	397	2.29	327
Spring - No data yet	-	-	-	-	-	-

<sup>a</sup>Data from Godish, 2004

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

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

Measure	HNO <sub>3</sub> ppbv	NH <sub>3</sub> ppbv	NH <sub>4</sub> ppb(w/w)	CO <sub>2</sub> ppmv	CH <sub>4</sub> ppmv	N <sub>2</sub> O ppbv
<i>Total downwind, avg</i>						
Height 1 (Top) <sup>a</sup>	1.60	39.1	0.37	404	2.28	327
Height 2	1.92	124.9	0.46	401	2.23	327
Height 3	1.65	246.9	0.47	405	2.35	327
Height 4	1.42	357.4	0.44	406	2.35	328
Height 5 (Bottom) <sup>a</sup>	1.63	426.9	0.52	414	2.47	329

<sup>a</sup>Measurement height varied with each data collection period based on climatic data. The top height is the highest collection height, and the bottom height, the lowest collection height.

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

### Future Work

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

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

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## A Boundary Layer Sampling Methodology for Measuring Gaseous Emissions from CAFOs

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### Introduction

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

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

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

### Methods

#### Set up

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

#### Validation

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

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

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

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

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

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

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

After collection, samples were injected equally into two evacuated vials for later  $\text{CH}_4$  analysis by GCMS.

## Results and Discussion

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

**Table 1. Climatic data summary for each sample period**

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

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

**Table 2. . Summary of filter pack performance**

<b>Measure</b>	<b>Collection, %</b>
Leak test efficiency, %	97.5
Ammonia recovery, %	97.7
	<b>Differentiation, %</b>
<i>Comparison of filter pack and denuder, %</i>	
Nitric acid	21.9
Ammonia	16.7
Ammonium	4.4

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

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

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

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

<sup>a</sup>Based on Gaussian plume calculations for ambient conditions

**Table 4. Summary of methane recovery data**

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

<sup>a</sup>Downwind is the total downwind concentration minus the background (upwind) methane levels.

## Conclusion

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



## **Determination of Particle (PM<sub>10</sub> and PM<sub>2.5</sub>) and Gas-Phase Ammonia (NH<sub>3</sub>) Emissions from a Deep-Pit Swine Operation using Arrayed Field Measurements and Inverse Gaussian Plume Modeling**

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### **Abstract**

The contribution of agricultural emissions of primary (direct) and secondary (precursor) pollutants to air quality is rapidly being recognized as an important fraction of local and regional air pollution budgets. However, a significant uncertainty still exists in the magnitude and rate of these types of emissions, especially under “in field” conditions common within the central and western United States. Described herein are the results of a study conducted at a deep-pit swine production facility in central Iowa. The facility consisted of three separate, parallel barns, each housing around 1,250 pigs with an average weight of approximately 90 pounds per animal. The area around the facility was topographically flat and surrounded by soybean and cornfields. A number of portable PM<sub>10</sub>/PM<sub>2.5</sub> (AirMetrics MiniVol) samplers and passive NH<sub>3</sub> (Ogawa Model 3300) samplers were arrayed vertically and horizontally around the three-barn production facility, and data were collected on a daily-averaged basis for approximately three weeks in August and September of 2005. Additionally, a monitoring station was established approximately 40 m to the north of the nearest barn to record the typical suite of meteorological parameters (wind speed, direction, temperature, etc.) for determination of near-source atmospheric advection and dispersion. The AirMetrics samplers were operated with PM<sub>2.5</sub> impactor separation heads for approximately the first half of the field study and were then switched to the PM<sub>10</sub> heads for the remaining portion of the study. Each AirMetrics sampler was fitted with a conditioned, preweighed Teflon filter and operated at approximately five liters per minute for a time-controlled 23-hour period. Following sampling, the filters were recovered, conditioned, and reweighed at USU’s Utah Water Research Laboratory (UWRL) in Logan, UT for filter catch and ultimate determination of each location’s PM<sub>2.5</sub>/PM<sub>10</sub> mass concentration. The Ogawa passive samplers were co-located and operated for the same time periods with the pre-treated (acid-coated) collection pads recovered after the same 23-hr period and stored appropriately until the final analysis for NH<sub>3</sub> concentrations could be performed via ion chromatography at the UWRL facility. Emission estimates were derived via the comparisons of the measured particulate and NH<sub>3</sub> concentrations at each sampling location with the concentrations for each receptor (sample) point found via application of the EPA-recommended ISCST3 air dispersion model (Lakes Environmental Software). The comparison of the measured and model predicted NH<sub>3</sub> concentrations resulted in a derived NH<sub>3</sub> emission rate of  $17.22 \pm 7.2$  g/pig/day. This value is slightly more than two times greater than referenced emission rates; however, the two emission rates are within statistical uncertainty of each other. The analyses for the particulate emissions are as yet incomplete; however, preliminary calculations show PM<sub>10</sub> and PM<sub>2.5</sub> emission rates of 0.55 and 0.14 g/pig/day, respectively.

### **Introduction**

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

The contribution of agricultural emissions of primary (direct) and secondary (precursor, especially ammonia) pollutants to air quality has only recently been recognized as an important fraction of local and regional air pollution budgets (Bicudo et al., 2002). However, a significant uncertainty still exists in the magnitude and rate of these types of emissions, especially under “in field” conditions common within the



central and western United States (CENR, 2000; FAO, 2001; CAEAFO, 2002). As such several local and regional agricultural emission projects have been reported over the last few years (Hoff et al., 2005; Heber et al., 2005; and others).

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

### Methodology

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

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



**Figure 1. Particle and  $NH_3$  samplers near pig barn**

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

Ambient ammonia concentrations were monitored via passive sampling monitors described by Roadman et al. (2003). The samplers consist of a citric acid-treated quartz fiber pad, a series of diffusion screens, an

inert housing, and a rain shield. The samplers were exposed at the arrayed locations for a recorded period of time and recovered into air-tight containers. The pads were then transferred to individual sampling bottles until they could be returned to USU for  $\text{NH}_3$  analysis using ion chromatography.

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

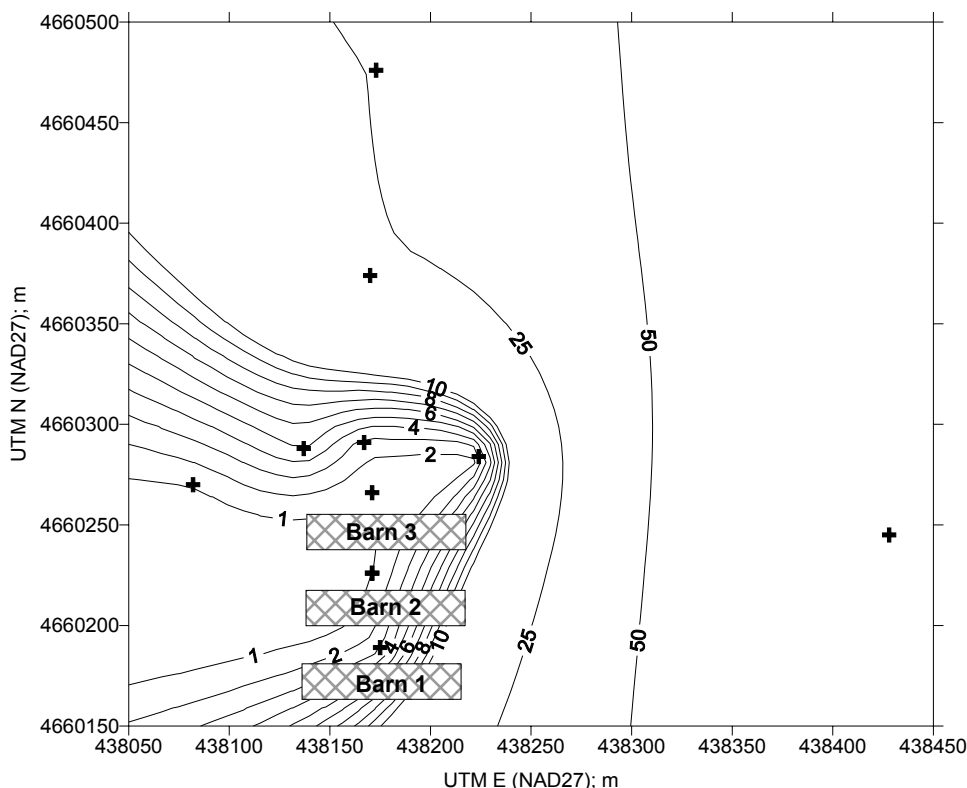
The pollutant concentrations, source/receptor locations and meteorology were used in conjunction with the U.S. EPA's Industrial Source Complex, Short Term (ISCST3) Gaussian plume dispersion model to back calculate the emissions required to observe the monitored pollutant concentrations. The specific software used was the ISC-AERMOD package marketed by Lakes Environmental Software. In brief, the model was operated for the chosen time period, using observed meteorology and a "seed" value for the initial emission rates. After several approaches it was determined that treating the barns as volume sources most reliably produced results similar to the observed concentrations. The initial emission rates were obtained from those reported by other investigators for similar facilities (Hoff et al.; 2005). The initial  $\text{NH}_3$  emission rate was assumed to be 7.43 g/pig/day, while the initial  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  emissions were assumed to be 0.11 g/pig/day and 0.028 g/pig/day (since no separate value was given for  $\text{PM}_{2.5}$ , its emission rate was assumed to be 25% of the  $\text{PM}_{10}$  rate). Modeled concentrations at the specified receptor (sampler) locations were then compared to the observed values. The ratio of the observed values to the modeled values were then compiled and used as a multiplier for the "seed" emission rate to derive the on-site specific value.

### Results and Discussion

The observed ammonia concentrations ranged from 6.8  $\mu\text{g}/\text{m}^3$  farthest or upwind from the barns to 905  $\mu\text{g}/\text{m}^3$  nearest the barns. Samplers that were determined to be upwind or completely crosswind from the source, and therefore not affected by barn-generated emissions, were treated as local/regional background samples and subtracted from the barn-impacted samples. The average  $\text{NH}_3$  background sample was found to be around 25.7  $\mu\text{g}/\text{m}^3$ . The elevated locations (met towers) generally showed lower concentrations than samplers posted on the same towers but at lower elevations.

Overall, the modeled  $\text{NH}_3$  concentrations were on the same order as the observed values, with a few notable exceptions. The model was unable to adequately account for plume buoyancy and nearly always under-predicted the concentrations at the elevated receptor locations. Furthermore, the concentrations predicted by ISCST3 for the upwind or crosswind areas were usually zero or much less than 1  $\mu\text{g}/\text{m}^3$ , which also led to much smaller values than observed for those receptors.

The under prediction of the modeled concentrations for the extreme receptor locations resulted in anomalously large concentration ratios (measured over modeled) for these fringe sites (see Figure 2). If all of the receptor/sample locations are included, the overall average  $\text{NH}_3$  concentration ratio was found to be  $44.0 \pm 52.6$  (the uncertainty represents the 95% confidence interval). This would mean that the derived emission rate would need to be 44 times the assumed "seed" emission rate of 7.43 g/pig/day.



**Figure 2. Isoplethic map of the overall averaged ratio of the observed  $\text{NH}_3$  concentrations to the modeled  $\text{NH}_3$  concentrations.**

A more realistic  $\text{NH}_3$  emission rate can be derived, however, if the elevated and non-plume receptor points are ignored. By discounting the under-predicted locations, essentially all points outside of the “6” isopleth in Figure 2, the average concentration ratio (measured to predicted) becomes  $2.32 \pm 0.96$ , which equates to an average emission rate of  $17.2 \pm 7.2$  g/pig/day. This value is higher than, but statistically indistinguishable from, that of Hoff et al. (2005).

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

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

## Conclusions

The approach of coupling field-arrayed concentration measurements and inverse Gaussian modeling proved to be a valid and reasonable approach for modeling gas-phase ammonia emissions from the examined three-barn, deep-pit swine finishing facility (3,750 total animals). The derived  $\text{NH}_3$  emission rate of  $17.22 \pm 7.2$  g/pig/day was slightly more than a factor of two greater than the referenced emission rate (Hoff et al., 2005), but within the range of statistical uncertainty.

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

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

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

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### **Abstract**

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



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

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### Abstract

The physical state of tropospheric ammonium and sulfate aerosol particles is modeled in this study using a 3-D chemical transport model (GEOS-CHEM). The state of these particles as aqueous or crystalline is predicted using rules based upon the extent of neutralization by ammonium and on relative humidity. Therefore, an effect of agricultural ammonia emissions is to regulate the phase of sulfate particles in the troposphere. The five particle tracers in the model include aqueous sulfate, aqueous ammonium, solid ammonium sulfate (AS), solid letovicite (LET), and solid ammonium bisulfate (AHS). Gas-phase precursors for the formation of both sulfate and ammonium are also included. The deliquescence relative humidities (DRH) for AS, LET, and AHS are 80%, 69%, and 40%, respectively. The crystallization relative humidities (CRH) for different extents of neutralization of the aqueous particles are based upon recent laboratory results. The modeling results for 2001 show that the sulfate burden by mass is partitioned as 43% solids as an average for the troposphere. The solids are 93% AS, 6% LET, and 1% AHS. 25% of the sulfate burden is present as AS in the boundary layer, 40% in the middle troposphere, and 65% in the upper troposphere. When performing a sensitivity study by increasing CRH up until it is equal to the DRH, the tropospheric solid burdens increase from 40% to 72% for AS, 2.6% to 3.6% for LET, and 0.3% to 1.8% for AHS. The partitioning between solid and aqueous particles affects radiative transfer and various chemical cycles such as  $\text{N}_2\text{O}_5$  hydrolysis and ultimately troposphere ozone. Implications of these results for aerosol direct radiative forcing are considered.



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

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### **Abstract**

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

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

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

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

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

### **Olfactory Anatomy**

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

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

Chemical odorants pass by the olfactory epithelium and are dissolved into the mucus at a rate dependent on their water solubility and other mass transfer factors. The more water-soluble the chemical, the more easily it is dissolved into the mucus layer. Sites on the olfactory cells, assisted by specialized proteins, receive the chemical odorant. The response created by the reception of a chemical odorant depends on the mass

concentration, i.e. the number of odorant molecules. Each reception creates an electrical response of the olfactory nerves. A summation of these electrical signals leads to an action potential. If this action potential has high enough amplitude (i.e. threshold potential), then the signal is propagated along the nerve where it synapses with the olfactory bulb.

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

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

### Laboratory Olfactometry

#### Overview of Odor Parameters

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

Four measurable, objective parameters of perceived odor are:

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

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

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

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

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

#### Odor Panels

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



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

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

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

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

### Determination of Odor Concentration in the Laboratory

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

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

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

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

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

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

is different from the other two, and a recognition response is that the selected presentation smells like something.



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

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

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

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

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

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

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

The odor concentration results from olfactometry testing are expressed as a detection or recognition threshold. The detection threshold (DT) is an estimate of the number of dilutions needed to make the actual

odor emission non-detectable. The recognition threshold (RT) represents the number of dilutions needed to make the odor sample faintly recognizable.

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

### International Standardization of Odor Concentration Measurement

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

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

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

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

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

### Odorous Air Dispersion Modeling

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

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

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

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

## Odor Intensity

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

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

## Odor Persistency

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

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

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

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

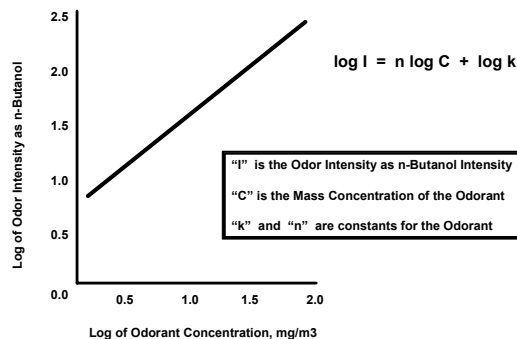
As an example, this expression means that there would be the same perceived increase in intensity when changing a concentration of sugar in water from 10% to 11% as when changing the concentration from 20% to 22%.

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

$$I = k C^n$$

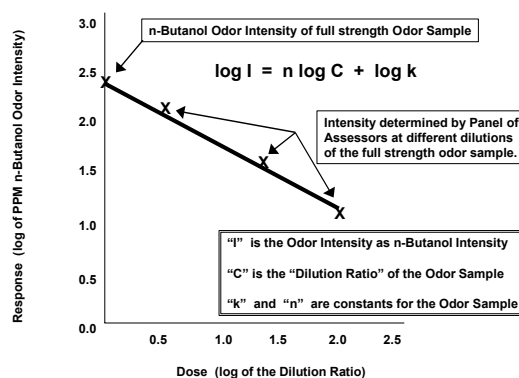
Where I is the odor intensity, C is the mass concentration of odorant (e.g. mg/m<sup>3</sup>), and k and n are constants that are different for every specific odorant or mixture of specific odorants.

As shown in Figure 2, this equation is a straight line when plotted on a log-log scale. The x-axis is the mass concentration (mg/m<sup>3</sup>) of the single odorant. The upward slope of the graph illustrates that the odor intensity of the single odorant increases as the mass concentration increases. Steven's Law has been used most often in modern odor science (Dravnieks, 1979; O'Brien, 1991; Prokop, 1992).



**Figure 2. Power law graph of a single odorant.**

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



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

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

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

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

### Odor Characterization

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

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

### Applicability of Laboratory Olfactometry

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

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

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

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

### Field Olfactometry

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

### Olfactory Performance of Odor Inspectors

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

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

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

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

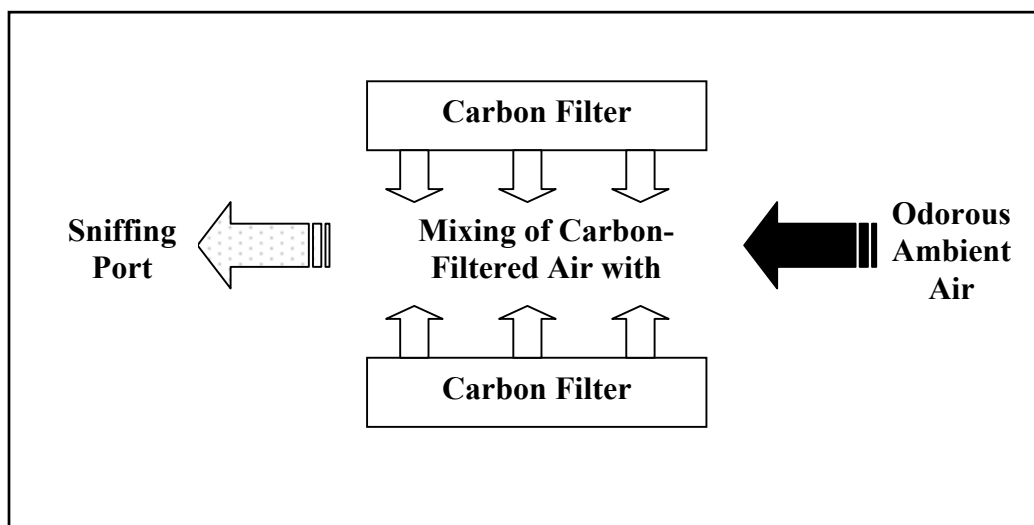
### Ambient Odor Concentration (D/T) with Field Olfactometers

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

manufactured by the Barnebey-Cheney Company and subsequently manufactured by the Barnebey Sutcliffe Corporation.

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

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



**Figure 4. Block diagram of field olfactometer air flow.**

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

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

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

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

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

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

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

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

### Scentometer Field Olfactometer

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



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

### Nasal Ranger Field Olfactometer

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

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

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





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

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

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

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

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

## Conclusions

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

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

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

With these standard odor measurement practices, odor limits may be incorporated into odor regulations or into facility permits as compliance determining criteria with confidence. This can be done with ambient odor limits based on odor concentration (D/T) or on source odor limits based on either the odor

concentration (odor units per cubic meter) or odor emission rates (odor units per second). Note that these basic odor limits are not mutually exclusive and are sometimes combined.

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

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## Agricultural Emissions of Greenhouse Gases in Croatia

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### Abstract

The Republic of Croatia is a signatory to the Kyoto Protocol. Upon its entering into force and its ratification by Parliament, Croatia shall commit to reduce its emissions of GHG by 5 percent in relation to the reference year, over the commitment period from 2008 to 2012. Agricultural activities contribute directly to emissions of greenhouse gases and are seen as a source with great potential in reducing them. Methane (CH<sub>4</sub>) and nitrous oxide (NO<sub>2</sub>) are the primary greenhouse gases emitted by agricultural activities. On the basis of the best available activity data, emissions were estimated for the period from 1990 – 2003, in accordance with methodology prescribed by the scientific body of the Convention (Intergovernmental Panel on Climate Change – IPCC).

## 1. Agricultural Methane (CH<sub>4</sub>) Emission

### 1.1. Methane (CH<sub>4</sub>) Emission – Enteric Fermentation

Methane is a direct product of animal metabolism generated during the digestion process. The greatest producers of methane from enteric fermentation in Croatia are ruminants (cows, cattle, and sheep). The amount of methane produced and excreted depends on the animal digestive system and the amount and type of the animal feed. Figure 1 shows the emission of methane from enteric fermentation for the period from 1990-2003. The estimates in this inventory include only emissions for farm animals. CH<sub>4</sub> emission from enteric fermentation is a key source, both by level and trend. Dairy cattle is the single major source of emissions represent more than 50% of total CH<sub>4</sub> emissions from enteric fermentation, followed by non dairy cattle represent about 30% of total CH<sub>4</sub> from enteric fermentation.

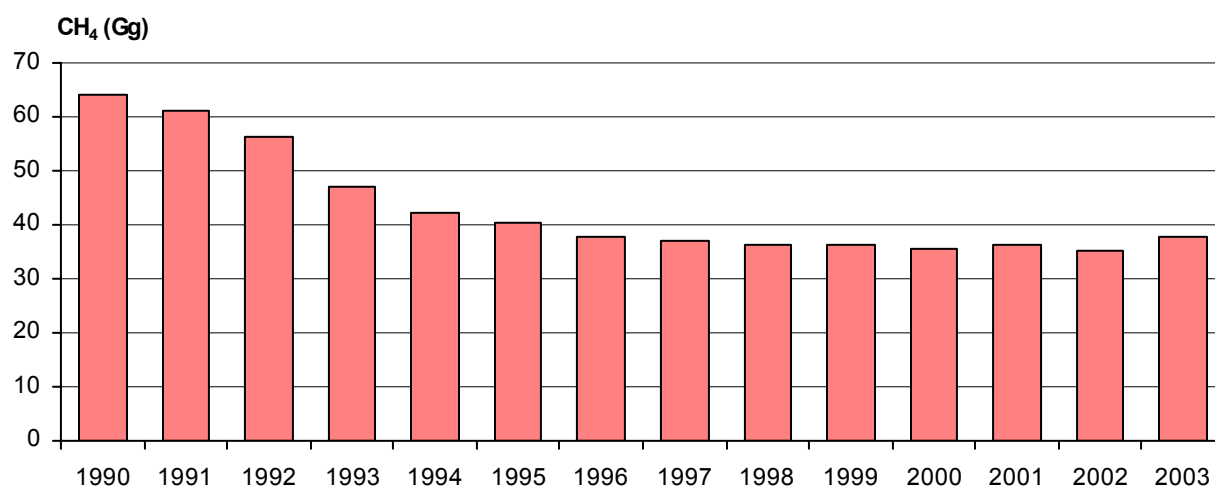
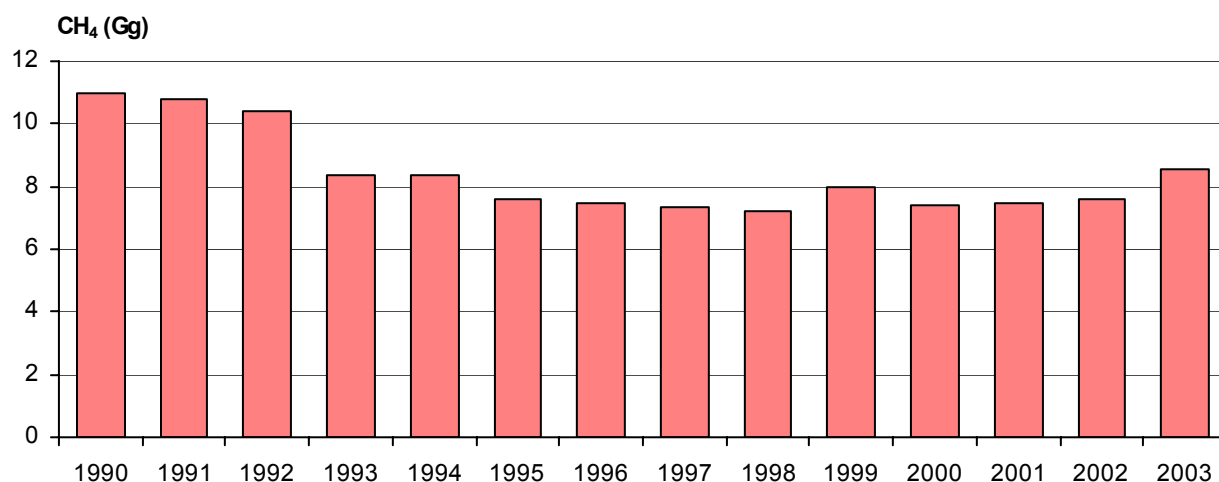


Figure 1 - CH<sub>4</sub> emission from Enteric fermentation (Gg)

### 1.2. Methane (CH<sub>4</sub>) Emission - Manure Management

Methane is generated under the conditions of anaerobic decomposition of manure. Storing methods of the manure in which the anaerobic conditions prevails (liquid animal manure in septic pits) are favourable for

anaerobic decomposition of organic substance and release of methane. Methane emission from manure management for the period from 1990 to 2003 is given in the Figure 2.

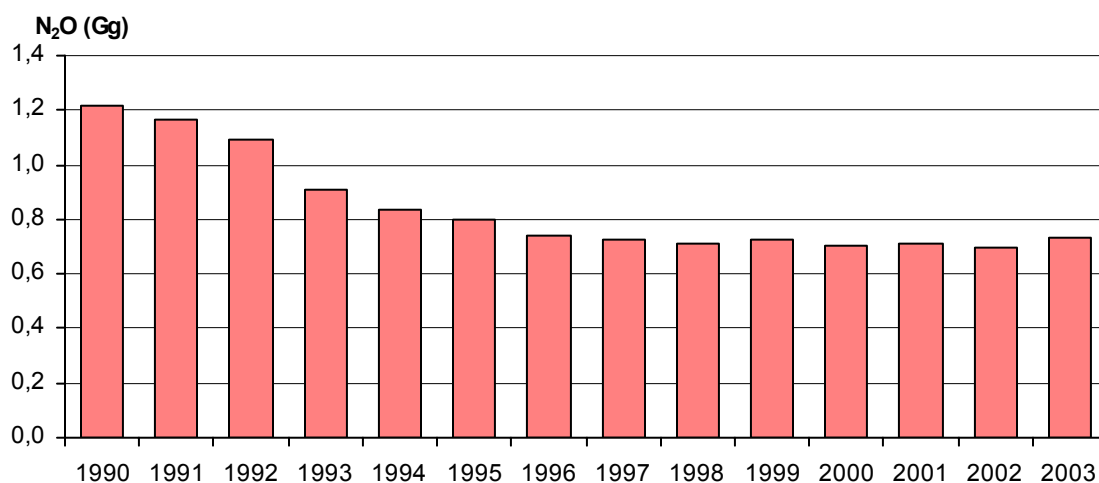


**Figure 2 - CH<sub>4</sub> emission from Manure Management (Gg)**

## 2. Agricultural N<sub>2</sub>O Emission

### 2.1. N<sub>2</sub>O Emissions from Manure Management

The emissions of nitrous oxide (N<sub>2</sub>O) from all animal waste management systems are estimated. This includes emissions from anaerobic lagoons, liquid systems, solid storage, dry lot, and other systems. The N<sub>2</sub>O emissions from pasture range and paddock are reported under Agricultural soils. The nitrous oxide (N<sub>2</sub>O) emissions from manure management for the period from 1990 to 2003 are shown on figure 3.

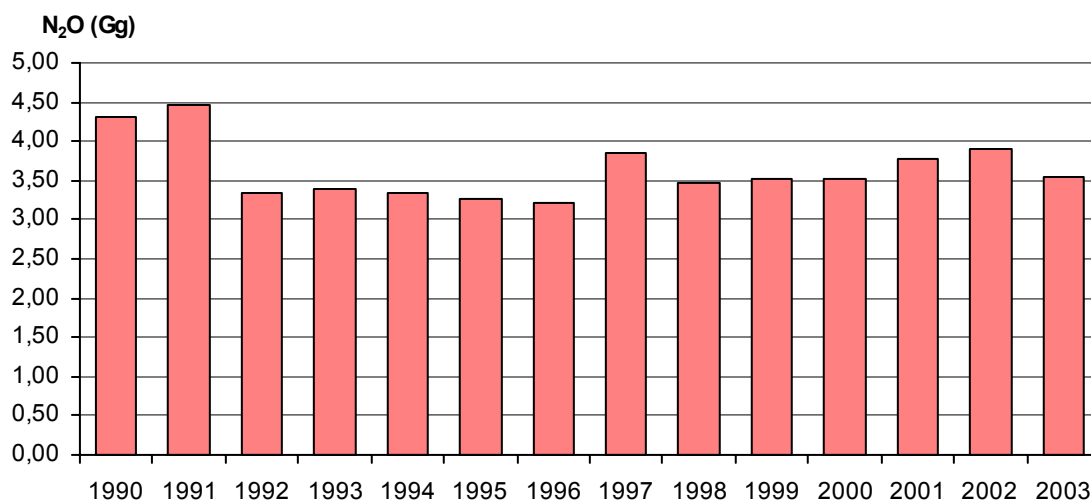


**Figure 3 - N<sub>2</sub>O Emissions from Manure Management (Gg)**

### 2.2. Direct N<sub>2</sub>O Emissions from Agricultural Soils

Direct emissions N<sub>2</sub>O from agricultural soils includes total amount of nitrogen applied to soils through cropping practices. These practices includes application of synthetic fertilizers, nitrogen from animal waste, production of nitrogen-fixing crops, nitrogen from crop residue mineralization, and soil nitrogen mineralization due to cultivation of histosols. The input data required for this part of the calculation were:

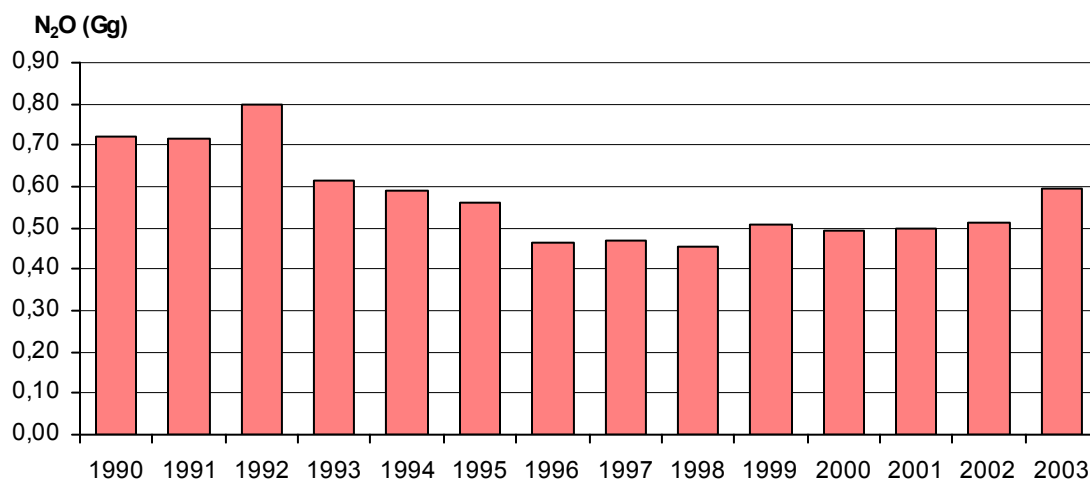
annual quantity of the synthetic fertilizer used, the quantity of organic fertilizer, the head of animals by its category, the biomass of leguminous plants and soybean, and the surface of histosols. Figure 4 shows direct emission of nitrous oxide from agricultural soils (1990 – 2003).



**Figure 4 - Direct N<sub>2</sub>O Emissions from Agricultural Soils (Gg)**

### 2.3. Direct Emission of N<sub>2</sub>O from Animals

Estimates of N<sub>2</sub>O emissions from animals were based on animal waste deposited directly on soils by animals in pasture, range and paddock. The same emission factor (0.02 kg N<sub>2</sub>O-N/kg of emitted N) suggested by IPCC (1996) was used for all grazing animals, regardless of their species and climatic conditions. Figure 5 shows direct emission of nitrous oxide from animals (1990 – 2003).

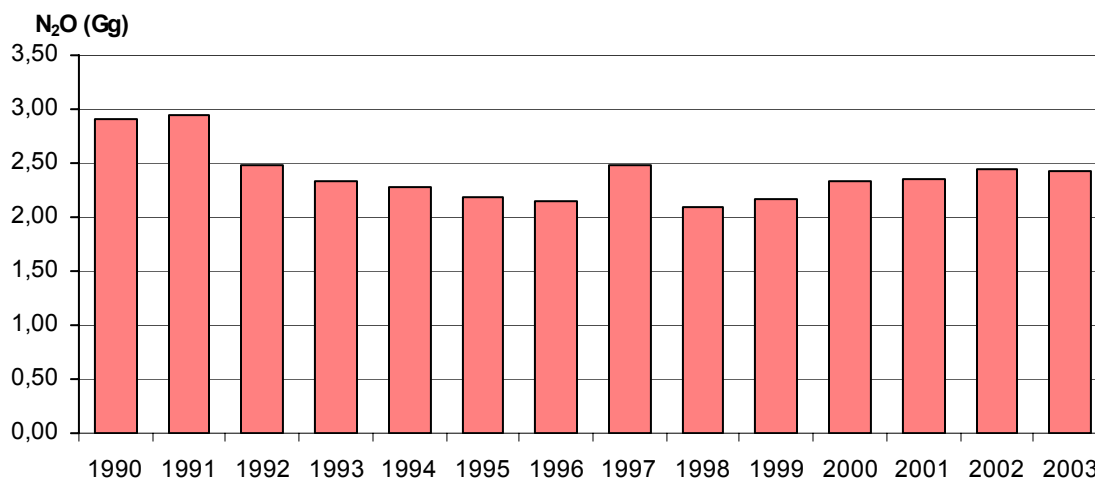


**Figure 5 - Direct N<sub>2</sub>O Emissions from Animals (Gg)**

### 2.4. Indirect N<sub>2</sub>O Emissions from Nitrogen Used in Agriculture

Calculations of indirect N<sub>2</sub>O emissions from nitrogen used in agriculture are based on two pathways. These are: volatilization and subsequent atmospheric deposition of NH<sub>3</sub> and NO<sub>x</sub> (originating from the application of fertilizers and animal manure), and leaching and runoff of the N that is applied to, or deposited on soils.

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



**Figure 6 - Indirect N<sub>2</sub>O Emissions from Agricultural (Gg)**

### 3. Conclusion

Methane emissions from enteric fermentation and manure management represent 41 percent of total CH<sub>4</sub> emissions (in year 1990.) from anthropogenic activities, respectively. Of all domestic animal types, dairy cattle were by far the largest emitter of methane. Agricultural soil management activities such as fertiliser application and other cropping practices were the largest source of Croatian N<sub>2</sub>O emissions, accounting for 70 percent of the total emission.

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

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

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### Abstract

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

### Introduction

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

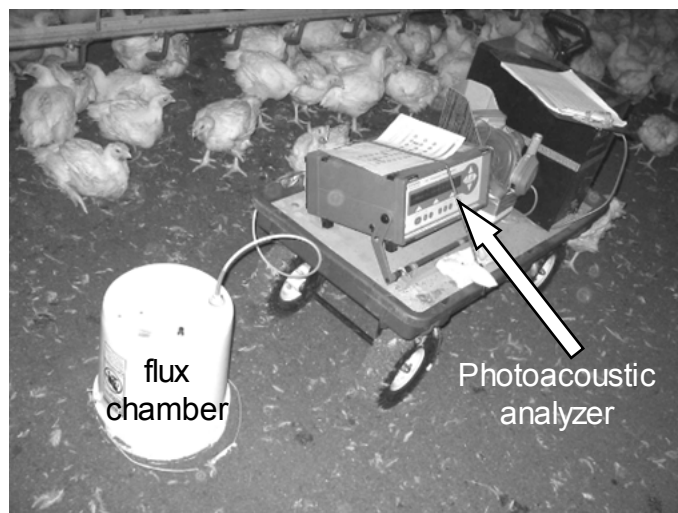
The objectives of this research were twofold: 1) to determine the magnitude of irregularity among litter parameters by intensive sampling and 2) to investigate the spatial variability of litter nutrients and litter gas flux within commercial broiler houses, hypothesizing those trends in variability could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

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



### Materials and Methods

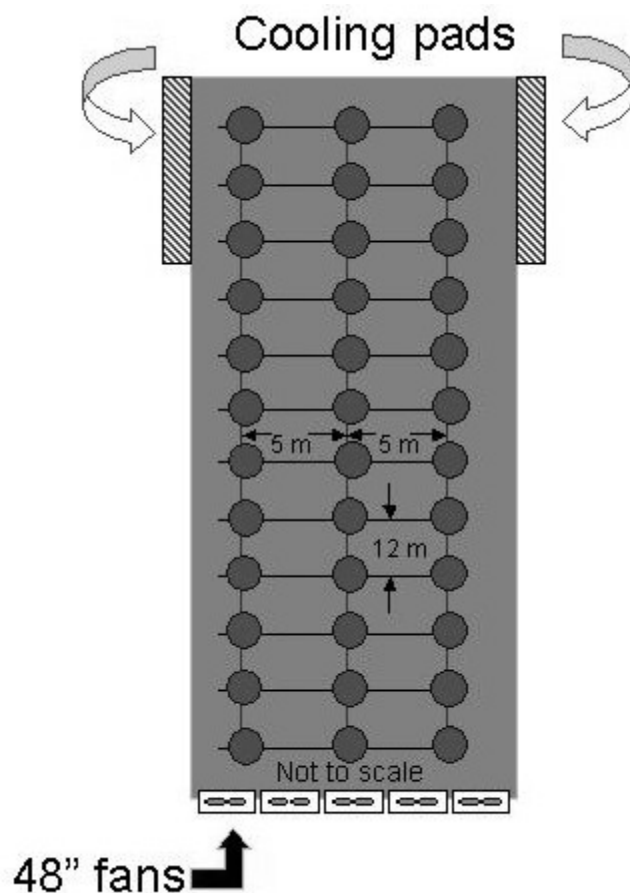
Twenty-four hours after chicks were placed in two solid sidewall commercial broiler houses (sampling day 2), litter samples were taken, chilled and transported to the laboratory for further analyses. Gas flux was estimated, at the same locations as litter sampling, using inverted plastic chambers and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



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

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

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



**Figure 2. Grid sample layout in broiler house.**

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

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

### Results and Discussion

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

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

Bird Age (day)	Location	Litter Properties		
		Temperature (C)	pH	Moisture (%)
2	H1	27.0 (18.3 to 44.2)	8.61 (8.31 to 8.85)	22.6 (13.4 to 33.0)
	H2	27.2 (18.3 to 41.4)	8.33 (6.58 to 8.90)	24.9 (12.3 to 32.1)
45	H1	27.8 (24.2 to 31.1)	8.43 (7.76 to 8.78)	29.5 (18.1 to 38.3)
	H2	27.6 (23.0 to 31.9)	8.00 (5.44 to 8.60)	36.4 (16.1 to 57.5)
		Litter Gas Flux (mg m <sup>-2</sup> hr <sup>-1</sup> )	Litter Nutrients (mg/kg)	
		NH <sub>3</sub>	NH <sub>4</sub>	NO <sub>3</sub>
2	H1	400 (149 to 769)	3631 (2020 to 5425)	1145 (409 to 2705)
	H2	307 (0 to 1151)	5109 (2769 to 13,143)	2350 (684 to 4336)
45	H1	694 (0 to 1455)	6184 (4341 to 8241)	110 (25 to 2136)
	H2	649 (0 to 1463)	7651 (3440 to 24,506)	89 (0 to 665)

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

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

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

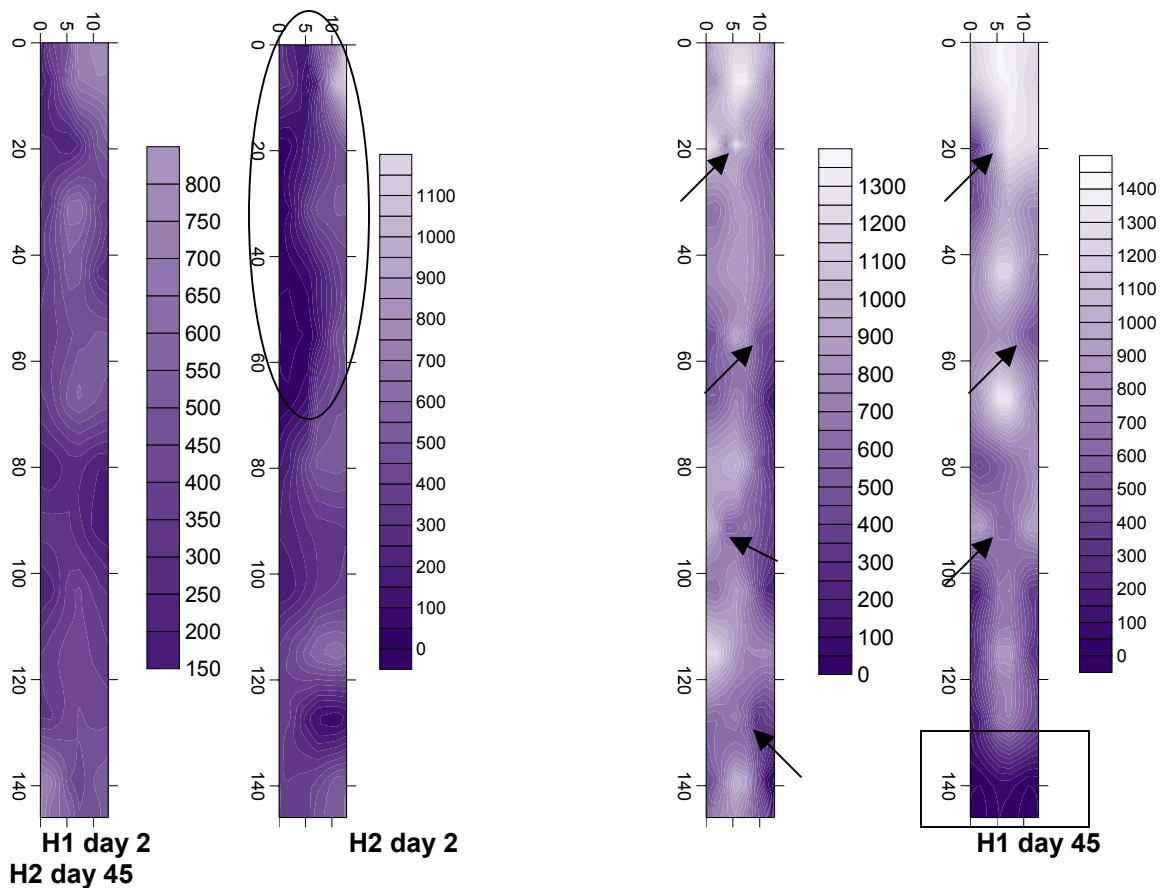
Variograms for ammonia flux over the floor area of the two houses are presented in Figure 3. The pair of plots on the left represent day 2, where the darker shading is indicative of lower ammonia flux. The oval around the brood area of H2 denotes the litter treatment area where the ammonia flux was essentially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

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

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

## Conclusions

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



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

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

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### Abstract

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

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

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

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

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

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

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

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

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

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

The total emissions for all measured organic carbonaceous gases (VOCs and methane) was clearly dominated by methane. When cows were present in the chambers, VOCs were less than one percent of total organic gas (TOG), which is a factor of 10 smaller than that historical and current emission estimates used

by the air regulatory agencies. A significant source of VOC emissions during the present studies were from feedstuff, namely alcohol emissions from silage. However, additional research is needed to quantify silage emissions and to compare emissions from different silage types.

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

Key Words: Dairies, Greenhouse Gas, Volatile Organic Compound



## Ammonia and Trace Gas Emissions from Organic Fertilizers Amended with Gypsum

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### Abstract

More than 2/3 of anthropogenic ammonia emissions (NH<sub>3</sub>) result from animal operations with most NH<sub>3</sub> deriving from urea excreted from cattle and swine and uric acid from poultry. NH<sub>3</sub> emissions are accompanied by emissions of nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>), trace gases with high impact on global warming and destruction of the stratospheric ozone layer. From experiments on paddy rice fields the inhibiting effect of sulfate on CH<sub>4</sub> emissions is known. In field trials as well negative correlations between N<sub>2</sub>O emissions from soils and soils sulfate contents were found. From this correlations the possibility of emission reduction through sulfate was deduced. First experiments about the general influence of gypsum (calcium sulfate) on both NH<sub>3</sub> and trace gas emissions from animal wastes were carried out. Emissions of these gases were measured in a lab experiment while broiler manure and liquid swine manure were stored in open vessels. Gas fluxes were measured daily with a multigas monitor. Contents of dry matter, NH<sub>4</sub>-N, and total N were determined from the animal wastes.

After 10 days of storage cumulative emissions from liquid swine manure reached 2,350 g NH<sub>3</sub>, 0.56 g N<sub>2</sub>O, and 5,680 g CH<sub>4</sub> per kg dry matter at maximum. Reduction of N<sub>2</sub>O and CH<sub>4</sub> emissions by addition of gypsum was as high as 62 % and 26 %, respectively.

From poultry manure cumulative fluxes after 10 days of storage were 487 g NH<sub>3</sub>, 25 g N<sub>2</sub>O, and 8,593 g CH<sub>4</sub> per kg dry matter at maximum. Reduction of NH<sub>3</sub> and CH<sub>4</sub> emissions was as high as 7 % both.

Emissions of N<sub>2</sub>O and CH<sub>4</sub> were up to 45times higher from poultry manure than from liquid swine manure while emission of NH<sub>3</sub> was more than 5times higher from liquid swine manure than from poultry manure (emissions per kg dry matter).

Effects in reduction are related to the dry matter contents of the investigated materials and the dry matter dependent existence of anaerobic microsites. High reduction effects in liquid swine manure which derive from addition of gypsum may be caused by anaerobic CH<sub>4</sub> oxidation and its connection to denitrifying processes including N<sub>2</sub>O formation and anaerobic NH<sub>3</sub> oxidation. Above all, it seems to be possible to reduce NH<sub>3</sub> and trace gas emissions from animal wastes by addition of gypsum.

### Introduction

Because of the clean air acts SO<sub>2</sub> emissions in western Europe are decreased drastically (Dämmgen et al., 1998). Thus macroscopic sulfur (S) has become a major limiting factor for plant production in industrialized as well as remote rural areas (Schnug & Haneklaus, 1998). On the other hand recent research has shown that sulfate reduces CH<sub>4</sub> formation because of substrat competition between sulfate reducing microorganisms and Methanogens (Corton et al., 2000; Wassmann et al., 2000; Gauci et al., 2004). Furthermore sulfate as part of sulfuric acid is used in waste air treatment systems to reduce NH<sub>3</sub> emissions from animal housing (Hahne & Vorlop, 2001). Model (2004) has found a positive relation between nitrate sulfate ratio in soils and nitrous oxide emissions from organic farming systems. That means that the more sulfate in relation to nitrate is found the less N<sub>2</sub>O is emitted.

With respect to all this positive impacts of sulfate in reducing gaseous emissions lab experiments were carried out to investigate the general influence of gypsum (calcium sulfate) on both NH<sub>3</sub> and trace gas emissions from animal wastes. Gypsum is one of a few mineral fertilizers allowed to use in organic farming.

## Methods

### Experiment I - Material

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

### Experiment II - Material

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

### Trace Gas Measurement

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

## Results and Discussion

### Experiment I

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

CH<sub>4</sub> emitted on a constant high level from the first until the last day of the investigation period (Figure 1B). Emission rates ranged between 42 g and 31 g CH<sub>4</sub> per kg dry matter and day with constant higher rates from control variant (up to 9.2 % per day). Constant high emission rates indicate a full microbial activity until the last day of measurement and thus the need for a longer investigation period. Cumulative fluxes after 10 days of storage were 8,593 g CH<sub>4</sub> from control variant and 7,977 g CH<sub>4</sub> per kg dry matter from gypsum amended variant (Figure 3). At least a reduction of CH<sub>4</sub> emission was observed as high as 7 %, too.

In opposite to NH<sub>3</sub> and CH<sub>4</sub> emissions highest N<sub>2</sub>O emission rates were observed at the last two days of investigation period (Figure 1C). At least N<sub>2</sub>O emission rates ranged between 102 and 89 mg per kg dry matter and day in both variants. Constant lower emission was observed from control variant (up to 14 % per day). 10 days after storage cumulative fluxes were 22 g N<sub>2</sub>O from control variant and 25 g N<sub>2</sub>O per kg dry matter from gypsum amended variant (Figure 3). In this case a reduction of N<sub>2</sub>O emission was not observed.

It's important to notice that cumulative N<sub>2</sub>O emission was orders of magnitude lower than CH<sub>4</sub> and NH<sub>3</sub> emissions, while NH<sub>3</sub> emission was only one order of magnitude lower than CH<sub>4</sub> emission. CH<sub>4</sub> and NH<sub>3</sub> emissions were highly positively correlated ( $R = 0.884$ ,  $p < 0.000$ ). On the other hand both CH<sub>4</sub> and NH<sub>3</sub> emissions were negatively correlated with N<sub>2</sub>O emission ( $R = -0.424$ ,  $p < 0.001$  and  $R = -0.404$ ,  $p < 0.001$ , respectively).

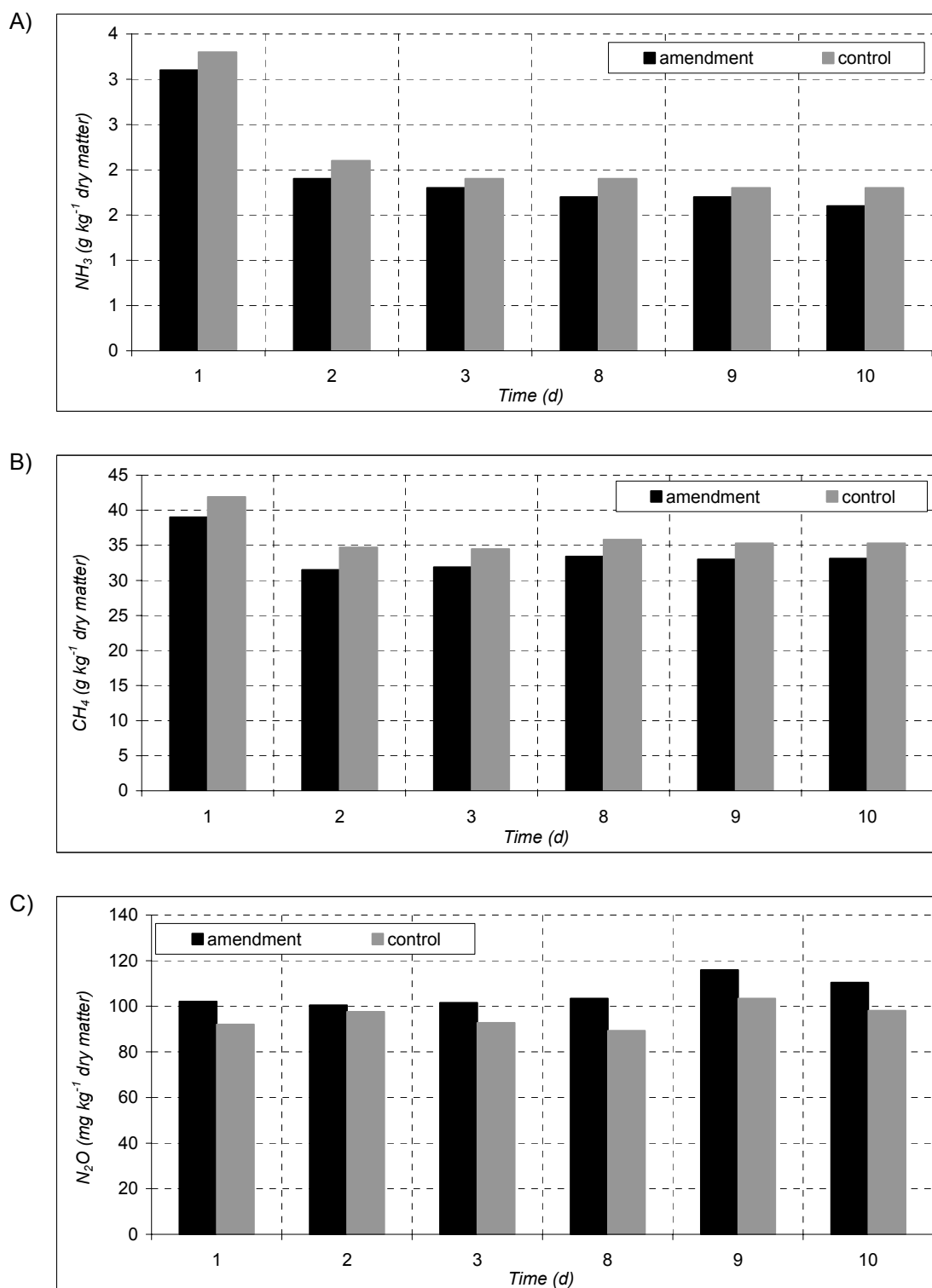


Figure 1: Gas fluxes from broiler manure

## Experiment II:

With respect to results in Experiment I gas flux measurement was done over a period of four weeks now. In this period  $\text{NH}_3$  emission rates ranged between 5.0 and 20.3 g per kg dry matter and day in both variants. Only the third rate of added gypsum led to constant lower emission rates from this variant in opposite to control variant (Figure 2A). The second rate of added gypsum induced only short term effect (day 8 in Figure 2A), and the effect of the first added rate was not measurable. So a clear reduction of  $\text{NH}_3$  emission by addition of gypsum was not found. Hence the question arises, what is the most effective application rate and in relation to which parameters it is best calculated. Cumulative fluxes after 10 days of storage were 2.3 kg  $\text{NH}_3$  from control variant and 2.4 kg  $\text{NH}_3$  per kg dry matter from gypsum amended variant, respectively (Figure 3). That means that  $\text{NH}_3$  emission from liquid swine manure was about five times higher than emission from broiler manure.

As like as with broiler manure  $\text{CH}_4$  emission was constant lower from gypsum amended variant (up to four times at day 23, see Figure 2B). In opposite to  $\text{NH}_3$  emission the effect of added gypsum is clearly to be seen. Each first day after addition (day 1, 9, and 23 in Figure 2B) the difference between emissions from both variants is greatest and then reduces with time. At the end of the whole measuring period the reduction of  $\text{CH}_4$  emission by addition of gypsum was as high as 27 % (8.1 kg in opposite to 11.0 kg  $\text{CH}_4$  per kg dry matter). After 10 days of storage cumulative fluxes reached 5.7 kg  $\text{CH}_4$  from control variant and 4.2 kg  $\text{CH}_4$  per kg dry matter from gypsum amended variant (Figure 3). That means that  $\text{CH}_4$  emission from liquid swine manure was nearly two times lower than from broiler manure.

In this experiment negative  $\text{N}_2\text{O}$  emission rates were calculated. In a first step technical problems in gas measurement could be excluded. In a next step it must be investigated if  $\text{N}_2\text{O}$  uptake into the manure or  $\text{N}_2\text{O}$  consumption could take place under lab conditions. Emission rates ranged between -10.5 mg and 70.0 mg  $\text{N}_2\text{O}$  per kg dry matter in both variants. With exception of the last two days the emission from gypsum amended variant was lower than from control variant. In cases of calculated  $\text{N}_2\text{O}$  consumption this was constant higher in gypsum amended variant. At the end of the whole measuring period the reduction of  $\text{N}_2\text{O}$  emission by addition of gypsum was as high as 71 % (2.5 g in opposite to 8.7 g  $\text{N}_2\text{O}$  per kg dry matter). After 10 days of storage cumulative fluxes reached 0.56 g  $\text{N}_2\text{O}$  from control variant and -0.21 g  $\text{N}_2\text{O}$  per kg dry matter from gypsum amended variant. That means that  $\text{N}_2\text{O}$  emission from liquid swine manure was negligible in comparison with broiler manure (Figure 3).

As like as with broiler manure cumulative  $\text{N}_2\text{O}$  flux was orders of magnitude lower than  $\text{CH}_4$  and  $\text{NH}_3$  emissions, while  $\text{CH}_4$  and  $\text{NH}_3$  were emitted in the same order of magnitude.  $\text{CH}_4$  and  $\text{NH}_3$  emissions were negatively correlated in this experiment ( $R = -0.621$ ,  $p < 0.000$ ). No correlation was found between  $\text{CH}_4$  emission and  $\text{N}_2\text{O}$  flux. On the other hand  $\text{N}_2\text{O}$  and  $\text{NH}_3$  fluxes were slight negatively correlated ( $R = -0.316$ ,  $p < 0.001$ ).

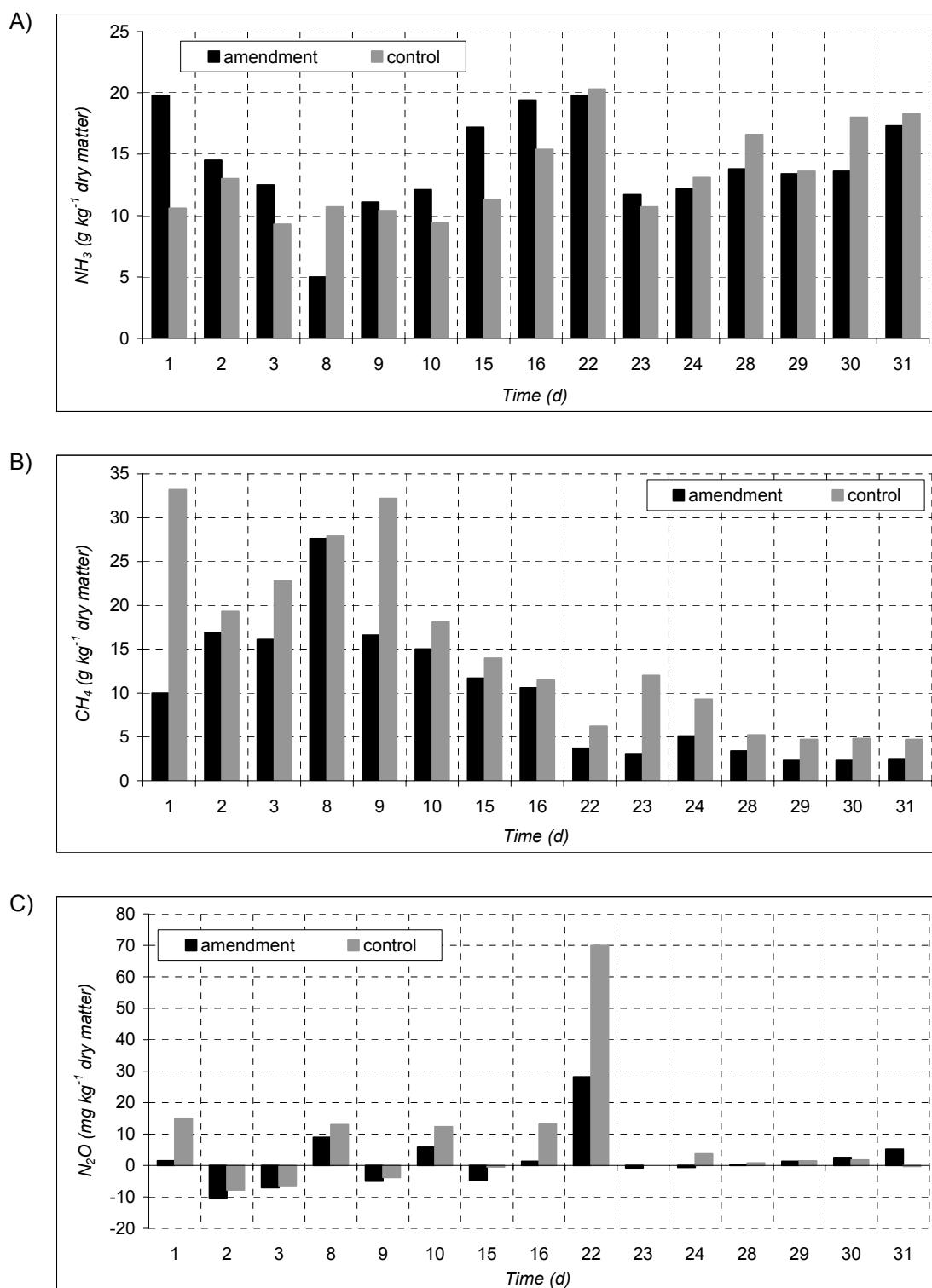
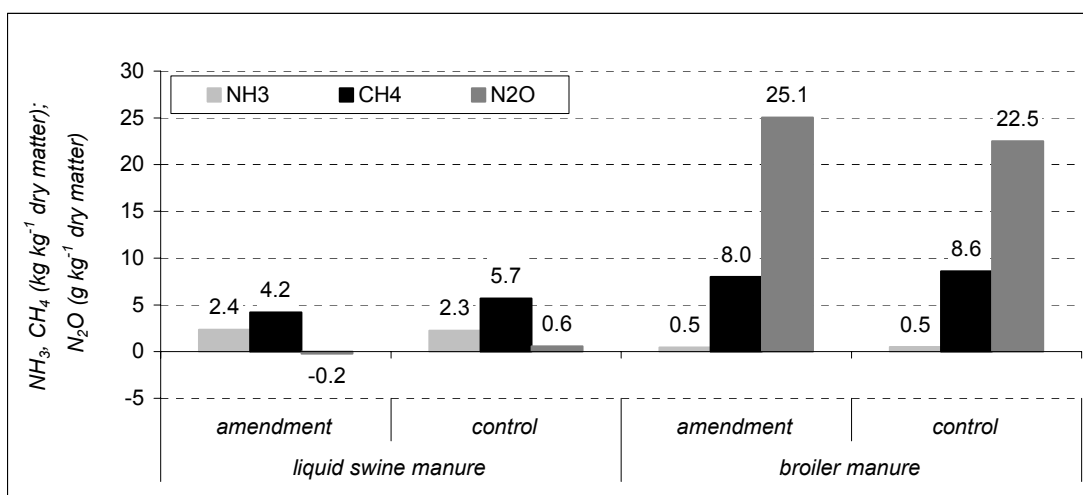


Figure 2: Gas fluxes from liquid swine manure

### Comparison between both experiments:

Data from CH<sub>4</sub> emission measurements are in good agreement with results described by Gauci et al. (2004) and Dise & Verry (2001). Both found a reduction of methane emission in sulfate amended plots (up to 30 %). Lower CH<sub>4</sub> fluxes as well as lower N<sub>2</sub>O fluxes from liquid swine manure might be caused by anaerobic CH<sub>4</sub> oxidation and its connection to denitrifying processes including N<sub>2</sub>O formation. Anaerobic CH<sub>4</sub> oxidation was described by Nauhaus et al. (2002) in marine sediments. Model (2004) describes the possible connection between anaerobic CH<sub>4</sub> oxidation and N<sub>2</sub>O formation for slurry treated soils. Because of more aerobic conditions in the broiler manure this processes might not occur with the same intensity as under anaerobic conditions in liquid swine manure. Higher NH<sub>3</sub> emissions from liquid swine manure are because of the higher NH<sub>4</sub>-N content than in broiler manure (4.2 g in opposite to 2.9 g per kg manure). Independent of single results the experiments indicate the general capability of reducing gaseous emissions from manure by addition of gypsum.



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

### Conclusions

There are already a number of investigations on mitigation strategies with most of them focussing on one gas only. They neglect the fact, that conditions reducing the emission of one trace gas might have a directly opposed effect on another (Wulf et al., 2001). By addition of gypsum it seems to be possible to reduce NH<sub>3</sub> as well as trace gas (CH<sub>4</sub>, N<sub>2</sub>O) emissions from animal wastes. In further experiments it is necessary to find out optimum application rates and conditions to provide best impact of sulfate addition.

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

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### Abstract

Nitrous oxide (N<sub>2</sub>O) is a greenhouse gas that contributes to radiative forcing of the atmosphere. Nearly 60 % of the N<sub>2</sub>O emitted into the atmosphere are released by natural as well as by agricultural and forest soils with 35,5 % by agricultural soils. The N<sub>2</sub>O gas flux from agroecosystems is highly dependent on management. Most important factors are fertilizer and/or manure application. To describe the influence of fertilizing/manuring it is usual to calculate fertilizer induced emissions. In this calculation background fluxes are involved. In the literature background fluxes used to discriminate fertilizer induced N<sub>2</sub>O emissions have been measured on plots without fertilizer application and are subtracted from emission rates measured on plots with fertilizer application. Problems of NH<sub>3</sub> emissions from organic fertilizers and its deposition onto adjacent unfertilized plots have been ignored, but could cause increased N<sub>2</sub>O emissions in the unfertilized plots. Above this mineralization rates in unfertilized plots are often higher than in fertilized/manured plots. Another problem is that the crops in unfertilized plots often differ from the fertilized crops (e.g. poplar tree plots versus rape or grassland plots and grassland plots versus wheat or potato plots). In this case the plant specific N uptake as well as the plant specific influence on soil microbiology through root exudates are ignored. Because of this problems unfertilized plots should not be used for the determination of background fluxes. A statistical method was developed to determine background fluxes from the fertilized/manured plots themselves. Data sets from longterm field experiments carried out near Leipzig and Potsdam were used. Background flux rates of N<sub>2</sub>O were calculated as mean values of emission rates in the range from 0 µg to <15 µg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup>. Most of them were observed in periods not influenced by any treatment (e.g. ploughing up of legumes, fertilizing/manuring). Instead of treatments they are influenced by the amount and the degradability of root and harvesting residues. For the plot near Leipzig a management-related background flux of 7,5 µg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup> was calculated. The background flux of the plot near Potsdam was in the same range.

### Introduction

The N<sub>2</sub>O gas flux from agroecosystems is highly dependent on management. Most important factors are fertilizer and/or manure application. To describe the influence of fertilizing/manuring it is usual to calculate fertilizer induced emissions (Bouwman, 1996; Simojoki & Jaakkola, 2000). In this calculation background fluxes are involved. In the literature background fluxes used to discriminate fertilizer induced N<sub>2</sub>O emissions have been measured on plots without fertilizer application and are subtracted from emission rates measured on plots with fertilizer application (Bouwman, 1996). Problems of NH<sub>3</sub> emissions from organic fertilizers and its deposition onto adjacent unfertilized plots have been ignored, but could cause increased N<sub>2</sub>O emissions in the unfertilized plots (Hellebrand & Scholz, 1997; Model, 2004). Above this mineralization rates in unfertilized plots are often higher than in fertilized/manured plots (Stahr et al., 1994; Beckmann et al., 2001). Another problem is that the crops in unfertilized plots often differ from the fertilized crops (e.g. poplar tree plots versus rape or grassland plots and grassland plots versus wheat or potato plots) (Teepe, 1998; Schmädeke, 1998; Kaiser & Ruser 2000). In this case the plant specific N uptake as well as the plant specific influence on soil microbiology through root exudates are ignored.

### Methods

#### Experimental Sites, Gas Flux Measurement

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



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

### Statistical Method for BFR Calculation

All measured emission rates were subdivided into classes with upper and lower borderlines which are shown in Table 1. In the first step the subdivision was independent from variants to get one value which characterises the background flux of the whole experimental site. Therefor a mean value was calculated from emission rates of those classes containing the most values. As an example in Table 1 the N<sub>2</sub>O emission rates of Spröda experimental site are given as in per cent per class (values in parentheses). In the next steps the subdivision was dependent on systems, variants or single crops.

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

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

Classes with upper borderlines ( $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ )									
<0 (4.1)	<5 (13.7)	<10 (17.6)	<15 (10.1)	<20 (7.5)	<30 (12.0)	<40 (9.7)	<50 (3.6)	<100 (11.1)	$\geq 100$ (10.3)

### Results and Discussion

At the Spröda experimental site in 21 per cent of all measurements N<sub>2</sub>O emission rates with more than 50  $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  were detected. 89 per cent of this emission rates were found in periods influenced by treatment measures, and about 6 per cent were found in winter time. In 33 per cent of all measurements N<sub>2</sub>O emission rates with more than 15  $\mu\text{g}$  but less than 50  $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  were detected. Half of this rates were found in periods influenced by treatment measures, too. Most N<sub>2</sub>O emission rates (42 per cent) ranged between 0  $\mu\text{g}$  and 15  $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ . Only 11 per cent of this rates were found in periods influenced by treatment measures. That means that emission rates of this range mostly were found in periods without any direct influence of manure application and ploughing up of legume grass, respectively. On the other hand the influence of site specific parameters might be stronger on processes resulting in N<sub>2</sub>O formation in this periods. Thus emission rates of this range were used to calculate management related background fluxes. This background flux was as high as 7.5  $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$ .

At the plot near Potsdam a management related background flux as high as 8.2  $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  was calculated. More than 50 per cent of all N<sub>2</sub>O emission rates were between 0  $\mu\text{g}$  and 15  $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  at this site. Most of them were found in periods not influenced by any treatment as well. This findings are in good agreement with results of Ruser et al. (1996). They describe a "background level" from 0-15  $\mu\text{g N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  as well in a fertilized crop but in periods without influence of fertilizer application.

Beside nitrate availability carbon availability is important in modification of N<sub>2</sub>O fluxes from soil (Firestone & Davidson, 1989; Aulakh et al., 1991; Benckiser, 1994). Soil respiration determined as CO<sub>2</sub> emission from bare soil characterises carbon availability as well as soil microbial activity (Schulz, 1986; Klimanek, 1988). The relation between carbon and nitrate is described by Umarov (1990) as  $\text{C}_{\text{org}} + \text{NO}_3 \rightarrow (\text{CH}_2\text{O})_n + \text{CO}_2 + \text{N}_2\text{O}$ . Hence it is not surprising that strong correlations between N<sub>2</sub>O and CO<sub>2</sub> emissions were found in a few investigations (Flessa & Beese, 1995; Parsons et al., 1991; Simojoki & Jaakkola, 2000).

Management related background fluxes of N<sub>2</sub>O and CO<sub>2</sub> depending on single crops are given in Table 2 for Spröda experimental site (for calculation of CO<sub>2</sub> background fluxes see Model, 2004). Furthermore in this table values are given for amounts of root residues, detected from Klimanek (1997) in long term field trials at different experimental sites. Both N<sub>2</sub>O and CO<sub>2</sub> background fluxes could be set in a descending order as

summer wheat > maize >= alfalfa grass > rye/vetch mix. The same descending order is to be found for the mineralizable root residues available from the previous crop. That means that highest amounts of mineralizable root residues are left in the soil by alfalfa grass and might be decomposed in the period of growing summer wheat. In that time where highest amounts of mineralizable root residues were available highest background fluxes of both N<sub>2</sub>O and CO<sub>2</sub> were found. On the other hand lowest background fluxes of both N<sub>2</sub>O and CO<sub>2</sub> were found in the same period in which lowest amounts of mineralizable root residues were available. This findings agree with results of Rosswall et al. (1989), Fauci & Dick (1994), and Singh & van Cleemput (1997). All of them found positive correlations between N<sub>2</sub>O as well as CO<sub>2</sub> emissions and the amount of root residues left in the soil.

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

	alfalfa/grass	summer wheat	rye/vetch-mix	maize
BF N <sub>2</sub> O	0.7	0.8	0.5	0.7
BF CO <sub>2</sub>	6.6	8.1	6.4	6.5
RR	10.8	1.4	2.4	2.4

BF N<sub>2</sub>O and CO<sub>2</sub> = Management-related background flux rate (kg N<sub>2</sub>O-N ha<sup>-1</sup> year<sup>-1</sup>; t CO<sub>2</sub>-C ha<sup>-1</sup> year<sup>-1</sup>); RR = mineralizable root residues (mean values t dry matter per ha, Klimanek, 1997)

### Conclusions

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

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## **A Scenario of Agricultural Air Emissions: Bangladesh Perspective**

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### **Abstract**

Bangladesh is situated in the South Asia a densely populated more than 150 million people live in this country. About 85% people of this country live on agriculture and about 35% of total GDP comes from this sector. Only 20-25% people of total live in urban area they used Natural gas for cooking. But rest of the people live in village or remote area and they burn Agricultural by product which mainly come from crops and animals like, Straw, Rice husk, Wheat straw, Jute plant, Corn husk, maize plant, wood and Cow dung for their cooking purpose. As a result, a huge amount of carbon dioxide (CO<sub>2</sub>), sulphur dioxide (SO<sub>2</sub>), Hydrocarbon (HC) are emitting in the air continuously. That why air is being polluting every where specially in the rural area and this amount is also increasing day by day due to increase of population. Consequently, Most of house wife are effected such type of diseases i.e. Asthma, Cough, Eye irritation, Headache, Skin diseases, and some times severe carcinogenic. Same phenomena also are occurred for the children as well. Besides, agricultural operations, those that raise animals and grow crops, can generate emissions of gases, particulate matter, and chemical compounds. For example, animals confined to a barn or area (rather than field grazing), produce large amounts of manure. Manure emits various gases, particularly ammonia into the air. This ammonia can be emitted from the animal houses, manure storage areas, or from the land after the manure is applied. In crop production, the misapplication of fertilizers, herbicides, and pesticides can potentially result in aerial drift of these materials.

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

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

### **Introduction**

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

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

### **Sources of Agricultural Air Emissions**

Fires are the major source of air pollution and can lead to severe problems if the smoke is inhaled for a period of time. These fires can either be forest fires, oil fires, burning of dried leaves in the backyard or as

in the case of rural areas, large-scale burning of agricultural waste. Other sources include industries and power plants located in these areas. Some sources of air pollution are described briefly in the below:

### 1) Direct Sources

- a) In Bangladesh, generally bullock/buffaloes driven ploughs are used for cultivating land. But nowadays, due to less payment (approx. \$1.5 for 0-12 hrs) of agricultural labor crisis is increasing in rural areas that are why agricultural machineries are more familiar to cultivators which are rapidly shifting to them. Another reason for this dramatic change may be that the use of machinery is more efficient in terms of time and budget. These are the reasons that agricultural machineries like power tillers, tractors, seed drill machines, weeding equipment, combine harvester are using widely. All these machines are driven by diesel. As a result, CO, HC, NO<sub>x</sub>, Sox, PM are emitted in the air.
- b) Another important source of air pollution in the rural area of Bangladesh is rural industrialization. In rice mills, for example, rice husk is widely used for boiling rice and CO, CO<sub>2</sub> and SPM are emitted in the atmosphere and polluting the air.
- c) Livestock farming is also responsible for air pollution. From animal urine and cow dung ammonia, hydrogen sulphide and other toxic gases mixed with air. Besides manmade methane which released from the bowels of ruminating farm animals and their manure comes from the agriculture sources. Agriculture is also the main source of artificial emissions of nitrous oxide which is caused by the soil bacteria transforming nitrogen from fertilizer and manure into nitrous oxide.
- d) Now a day's small scale biomass plant is going to be familiar in the rural area to meet up their electricity demand where a huge amount of cowdung is using for this purpose. Consequently, a lot of methane is produced during these activities and thus contribute major effects of air pollution and also increase the green house gases in the atmosphere.
- e) During cultivation of land soils are broken down thus releases carbon dioxide into the atmosphere. Similarly fertilizer and manure management practices in the field may emit nitrous oxide that is an important greenhouse gas. Greenhouse gas methane is also released to the atmosphere during the storage and the application of livestock manure in the field.
- f) During cultivation of dry land dust particle dissimilates in the air thus have great negative impacts of health because airborne particulates directly penetrate into the lungs.
- g) When pesticides are applied in the field some times it may be responsible for polluting air because pesticide droplets are drift onto the adjoining areas during unrest weather conditions.

### 2) Indirect Sources

- a) In Bangladesh people in the rural areas burn agricultural residues, twigs, rice husks, wood, wooden dust, leaves, jute sticks, dried cow dung, and sometimes cow dung stick (jute stick inside surrounded by cow dung and then dried in the sun). These sticks are usually burned for cooking purposes. By burning these types of agricultural materials Suspended Particulate Matter (SPM), Carbon Monoxide (CO), and Volatile Organic Compounds (VOC) are emitted in the air. As a result, people, particularly women and children, suffer various complex diseases. In general, people in the rural areas burn agricultural residues, leaves, rice husk etc material outside their kitchens during the winter season (late October to March). The rest of the year, they do it inside their kitchens.
- b) During the morning time in winter season, it is a common practice in the rural area to make fire with straws and dried leaves and shake their hands and legs by sitting around the fire to protect them from cold. From these fires a significant amount of pollutants like particulate matter, carbon monoxide, nitrogen oxides, and VOC's are emitted. Consequently, people suffer of complex diseases. This nitrogen oxide contributes to the production of greenhouse gases.



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

### **Impact of Air Pollution on Health**

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

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

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

### **Health Impact of Specific Air Pollutants**

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

**Tobacco smoking:** Tobacco smoking is a common practice for the person of rural area in Bangladesh. Everyday specially when they works in the field they take tobacco and often they smoke cigarette( locally called *Biri*).Tobacco smoke generates a wide range of harmful chemicals and is a major cause of sick

health, as it is known to cause cancer, not only to the smoker but affecting passive smokers too. It is well-known that smoking affects the passive smoker (the person who is in the vicinity of a smoker and is not himself/herself a smoker) ranging from burning sensation in the eyes or nose, and throat irritation, cancer, bronchitis, severe asthma and a decrease in lung function.

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

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

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

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

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

**Ozone (O<sub>3</sub>):** Exposure to this gas makes our eyes itch, burn, and water and it has also been associated with increase in respiratory disorders such as asthma. It lowers our resistance to colds and pneumonia.

**Oxides of nitrogen (NO<sub>x</sub>):** This gas can make children susceptible to respiratory diseases in the winters.

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

**Sulphur dioxide (SO<sub>2</sub>):** Sulphur dioxide in the air is caused due to the rise in combustion of fossil fuels. It can oxidize and form sulphuric acid mist. SO<sub>2</sub> in the air leads to diseases of the lung and other lung disorders such as wheezing and shortness of breath. Long-term effects are more difficult to ascertain as SO<sub>2</sub> exposure is often combined with that of SPM.

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

### Legal frame

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

### Conclusions

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

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## The Relationship Between Agriculture and Atmospheric Chemistry: A Historical Perspective

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### Abstract

This paper will present an overview related to changing aspects concerning air composition and agriculture within the last 150 years and near future, which are twofold: first inspiring atmospheric chemistry research and now becoming a dominating controller of atmospheric chemistry. The discovery of the main constituents of our atmosphere (nitrogen and oxygen) was in relation with the beginning understanding of combustion processes around 1790. However, already before it has been found (Mayow, Hales, Senebier) that air contains a substance ( $\text{CO}_2$ ) which is essential for plant growth. Soon after discovering of oxygen (Priestley, Scheele, Cavendish, Lavoisier) it was seen that plants “restore” bad air. Soon later Ingenhousz and Saussure found that plants take up for growing not only water from soil but among carbon still other compounds from air. Boussingault first showed that nitrogen is incorporated from the atmosphere. Liebig, who is regarded to be the founder of modern agricultural chemistry, pointed out without doing experiments that this compound is ammonia. However, already a hundred years before (1733), Woodward proposed fertilizing with minerals. The early idea that plant growth is linked with atmospheric matter exchange indeed stimulated research in atmospheric chemical composition. Ammonium has been found in rain water around 1850 and even in air but not until beginning of 20<sup>th</sup> century analysed in its gaseous form. According to investigations by Robert Angus Smith, the atmospheric  $\text{NH}_3$  concentration in and around cities must be several times larger in that time than today, probably due to decomposition of biogenic waste and still missing sanitary conditions like canalisation. The demand for increasing agriculture yield resulted in mineral fertilizing. The consequence, however, an interruption of a balanced biosphere-atmosphere budget, has been recognized only in the 2<sup>nd</sup> half of 20<sup>th</sup> century. Now agricultural emissions became first into interest of buffering acid rain (but possibly acidifying soils), later into an overloading the nitrogen cycle (eutrophication) and finally into the climate change issue (greenhouse effect). Nowadays and in future, emissions from agriculture will play a dominant role in atmospheric chemistry. With decreasing industrial emissions (e.g.  $\text{SO}_2$ ,  $\text{NO}_x$ , VOC) agricultural emissions will play an increasing role in future atmospheric chemistry: ozone formation from  $\text{CH}_4$ , acidity budget from  $\text{NH}_3$ , particulate matter from soil dust. Based on own monitoring results, these topics will be illustrated.



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

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### **Abstract**

Excessive loads of some volatile forms of N (e.g.  $\text{NH}_3\text{-N}$ ,  $\text{N}_2\text{O}$ ) may have negative effect on the environment and public health. Animal production systems appear to be a large source of  $\text{NH}_3\text{-N}$ . This study estimated N volatilization based on the nitrogen to phosphorus ratio, extrapolated from a dataset of manure analyzed in laboratories located in Minnesota, Pennsylvania and Wisconsin. Animal categories evaluated included broilers, dairy cows, finishing swine, and laying hens. Annual N losses were 0.21 Tg, 0.42 Tg, 0.51 Tg, and 0.60 Tg for laying hens, milking cows, finishing swine, and broilers, respectively. These figures are likely to represent N lost from animal housing and manure storage only, i.e. field losses were not included. Nonetheless, estimated annual N losses were near or well above  $\text{NH}_3\text{-N}$  emission factors published in EPA (2004).

### **Introduction**

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

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

### **Materials and Methods**

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

### **Results and Discussion**

Given the source of manure analyses, N:P estimates are likely to represent N volatilization losses occurring from excretion until manure samples were collected. That occurred most probably while manure storage facilities were emptied and immediately before manure was spread onto fields. Farmers often send manure

samples to be analyzed in order to adjust a fertilization program to appropriately supplement crops demands. Estimated N loss per head (Table 1) was highest with dairy cow manure ( $127 \text{ g cow}^{-1} \text{ day}^{-1}$ ) and lowest from broiler litter ( $1.65 \text{ g bird}^{-1} \text{ day}^{-1}$ ), but total animal numbers offset the disproportions among animal categories. Annual N losses extrapolated from the dataset were 0.21 Tg, 0.42 Tg, 0.51 Tg, and 0.60 Tg for laying hens, milking cows, finishing swine, and broilers, respectively. It is important to note that N:P estimates did not consider potential losses occurring after manure application to the fields while EPA  $\text{NH}_3\text{-N}$  emission factors include the entire animal production system (housing, storage and manure application). Thus, figures shown in the Table 1 indicated  $\text{NH}_3\text{-N}$  emission factors (EPA, 2004) were much lower than N:P estimated N losses for swine and poultry but not dairy cows.

There should be little opportunity for denitrification within animal housing, where most N should be lost as  $\text{NH}_3\text{-N}$ . A larger proportion of N loss appears to originate from housing facilities in dairy production systems (Moreira and Satter, 2006; Moreira and Satter, 2005). There is evidence that denitrification (43% of N lost) may occur with highly diluted swine manure releasing  $\text{N}_2$  from lagoons (Harper et al., 2004). Nonetheless, it is still unknown whether denitrification occurs at similar rates from less diluted dairy manure in storage facilities. A near match between EPA and N:P estimated figures was possibly because most N is lost as  $\text{NH}_3\text{-N}$  from dairy manure. The larger proportions of  $\text{N}_2$  may have accounted for the large disparities found for finishing swine and poultry.

### Conclusion

This study showed that annual N losses were near or well above  $\text{NH}_3\text{-N}$  emission factors published in EPA (2004). The N:P can be used as an alternative to the mass balance approach whenever manure is contained within the facilities but weighing is impossible or impractical. The N:P technique can be used as a screening method to rank manure management practices according to their potential for N conservation.

### Acknowledgement

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

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

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

<sup>1</sup>  $[1 - (N:P_{\text{man}} \div N:P_{\text{exc}})] \times 100$ , where subscript "man" is manure and "exc" is excreta.<sup>2</sup>  $[1 - (N:P_{\text{man}} \div N:P_{\text{exc}})] \times N_{\text{exc}}$ , where subscript "man" is manure and "exc" is excreta.<sup>3</sup> US N volatilized: estimation extrapolated from manure analyzed in laboratories located in Minnesota, Wisconsin, and Pennsylvania.<sup>4</sup> Sum of N volatilization from poultry manure (laying hens plus broilers).<sup>5</sup> Percent of EPA (2004).

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

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### Abstract

There is a need for a robust and accurate technique to measure ammonia (NH<sub>3</sub>) emissions from animal feeding operations (AFOs) to obtain reliable emissions data and to develop abatement strategies. Two consecutive seasonal studies were conducted and ammonia emission rates (ERs) were estimated from an open-lot dairy in central Texas. Data including NH<sub>3</sub> concentrations were collected and ammonia emission fluxes (EF<sub>l</sub>) and ERs were calculated for the open-lot dairy in summer and winter of 2005.

A protocol using flux chambers was used to determine these NH<sub>3</sub> emissions from the open-lot dairy. Ammonia concentration measurements were made using chemiluminescence-based analyzers. The ground level area sources (GLAS) including open lots (cows on earthen corrals), separated solids, primary and secondary lagoons and milking parlors were sampled to estimate NH<sub>3</sub> emissions. Preliminary assessment of summer and winter data indicated that overall NH<sub>3</sub> emission rates were  $41.9 \pm 3.2$  kg.day<sup>-1</sup> for the summer and  $18.6 \pm 3.1$  kg.day<sup>-1</sup> for the winter season. The estimated emission rate for winter was approximately 45% lower than summer emission rates. Lagoons (62%) in summer and open-lot corrals (89%) in winter were the highest contributors to NH<sub>3</sub> emission for the open-lot dairy.

The difference between the overall emission rates from each season was due to ambient and source temperature variations, and loading rates of manure on GLAS. Higher NH<sub>3</sub> ERs were estimated in summer time as compared to the winter time in the open-lot dairy. There was spatial variation of NH<sub>3</sub> emission from the open lot earthen corrals due to variable animal density within feeding, shaded and dry areas of the open lot. This spatial variability was attributed to dispirit manure loading within these areas.

### Introduction

In both Europe and United States, the largest sources of ammonia emission are livestock and poultry operations and they account for an estimated 70-90% of total emissions. Cattle including dairy cows are the largest of animal sources contributing to NH<sub>3</sub> emissions. Atmospheric NH<sub>3</sub> is considered to be a precursor to PM<sub>2.5</sub>, one of the 6 USEPA criteria air pollutants. It is anticipated that NH<sub>3</sub> emissions from animal feeding operations (AFOs) in the US maybe be regulated in the near future.

Recommendations for future NH<sub>3</sub> research from AFOs, including measurement techniques to establish emission factors will be necessary to develop mass balance-based models. Development of emission factors using an isolated flux chamber (FC) method will bring new insights and confidence on determining science-based NH<sub>3</sub> emission factor from livestock and poultry. Information on seasonal NH<sub>3</sub> emissions variations at ground level area sources (GLAS) from dairy operations will assist with evaluation and selection of best management practices to control and abate such emissions.

The isolated flux chamber (FC) is one of the direct measuring techniques for surface gas emissions such as NH<sub>3</sub>. The USEPA has published a protocol using this method for GLAS emissions (Gholson et al., 1989). The technology is also applicable to liquid surfaces.

In our study, a flux chamber protocol was used to determine NH<sub>3</sub> emission rates from different ground level area sources in an open-lot dairy.

Two open-lots were randomly selected to represent the entire lot area. In addition, GLAS including primary and secondary lagoons, milking parlor facility and separated solids were sampled for NH<sub>3</sub> emissions during summer and winter conditions. NH<sub>3</sub> emission rates were calculated using real time NH<sub>3</sub> concentration and flux data.

Results of  $\text{NH}_3$  emission from open-lot dairy are presented. Discussion includes seasonal effects and spatial effects on  $\text{NH}_3$  emissions from GLAS at the open-lot dairy.

### Materials and Methods

An open-lot dairy (Fig. 1) in central Texas was selected to estimate  $\text{NH}_3$  emissions using a USEPA approved flux chamber measurement protocol. A description of the site is given below.

#### Open-lot Dairy

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

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



**Figure 1. Sampled Open-lot Dairy.**

#### Isolation Flux Chamber Sampling Protocol

Real-time samples from free-stall and open-lot dairy were collected continuously using isolation flux chamber method to determine the emission rates of  $\text{NH}_3$  from different GLAS. Isolation flux chambers have been used to measure emission fluxes of volatile organic compounds (VOCs) and inorganic gaseous pollutants from a wide variety of sources (Eklund, 1992). The design of the flux chamber includes an acrylic hemispherical top (dome) and a stainless steel cylindrical skirt. Odotech Incorporated supplied the hemispherical top for use in this research (Odotech Inc. Montreal, Canada). Mukhtar et al. (2003) have described the flux chamber used in this study.

#### Measurement of Ammonia Concentrations

On-site measurements for these studies were conducted by using a mobile laboratory. The mobile laboratory included  $\text{NH}_3$  analyzers, air flow mixing devices, a multiplexer system including mass flow controllers, a zero air generator, gas cylinders and power generators for electricity.

A chemiluminescence analyzer (Model 17C, Thermo Environmental Instruments, TEI, Massachusetts.) was used to measure  $\text{NH}_3$  for real time and continuous sampling.

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

### Ammonia Flux and Emission Rate Calculations

To estimate the emission rates, mass concentrations and emission flux values must be known. Measured  $\text{NH}_3$  concentrations were converted into mass concentrations ( $C_{\text{mass}}$ ). Emission rates were calculated for each individual GLAS using equation (2).

Once the concentration in mass per volume was determined, equations (1) and (2) were used to calculate  $\text{NH}_3$  flux and rate, respectively:

$$EFl_{\text{NH}_3} = \frac{C_{\text{mass}} \times V_{fc}}{A_{FC}} \dots\dots\dots (1)$$

where

- $C_{\text{mass}}$  = Mass concentration, ( $\mu\text{g}/\text{m}^3$ )
- $EFl_{\text{NH}_3}$  =  $\text{NH}_3$  gas emission flux ( $\mu\text{g}/\text{m}^2\text{-s}$ )
- $V_{fc}$  = Volumetric flow through the flux chamber ( $\text{m}^3/\text{s}$ )
- $A_{FC}$  = Area of flux chamber ("footprint",  $0.192 \text{ m}^2$ )

$$ER = EFl \times A_{sc} \dots\dots\dots (2)$$

where:

- ER = Emission rate, kg/day.
- $EFl_{\text{NH}_3}$  =  $\text{NH}_3$  gas emission flux ( $\mu\text{g}/\text{m}^2\text{-s}$ )
- $A_{sc}$  = Area of source (GLAS),  $\text{m}^2$ .

Measured  $\text{NH}_3$  concentrations (in ppm) were corrected for  $\text{NH}_3$  adsorption through the flux chambers. The procedure for accounting for adsorption losses has been described by Capareda et al. (2005).

### Data Analysis Process for Open-lot Dairy

At the open-lot dairy, each corral had areas (dry, shaded and feeding areas) of different cow density and hence varying manure (feces and urine) loading rates. In the summer time, dry area within the corral was marked by minimum cow activity and manure loading while the feeding area had the highest cow activity and manure loading. In the winter time, during  $\text{NH}_3$  emission sampling, no one area within the corral was observed to be higher or lower in cow density. The open-lot corral  $\text{NH}_3$  data was highly spatially variable for both seasons. A log transformation was used and the data resulted in a normal distribution. After transformation of these data, an F-test on the normalized  $\text{NH}_3$  concentrations was performed to assess significant differences among dry, shaded and feeding areas of these corrals. Ammonia concentrations measured from other GLAS at open-lot dairy had normal distributions and therefore, no transformation of these was performed.

### Results and Discussion

In 2005, 115 and 109  $\text{NH}_3$  concentration samples were collected from the open-lot dairy GLAS in summer and winter seasons, respectively. This dairy had 12 earthen corrals for milking cows. Each corral had similar total area ( $8570 \text{ m}^2$ ). In both studies, one corral was randomly chosen to represent all open lots at the dairy. Approximately 170 milking cows were fed in the sampled corral. Preliminary assessment of summer and winter data indicated that overall  $\text{NH}_3$  emission rates were  $41.9 \pm 3.2 \text{ kg.day}^{-1}$  for the summer and  $18.6 \pm 3.1 \text{ kg.day}^{-1}$  for the winter season. The estimated  $\text{NH}_3$  emission rate for winter was nearly one half (45%) of that from summer. Lagoons (62%) in summer and open-lot corrals (89%) in winter were the highest contributors to  $\text{NH}_3$  emission for the open-lot dairy. The difference between the overall emission rates from each season was due to ambient and source temperature variations. Spatial variation of  $\text{NH}_3$  emission from the open lot earthen corrals was due to different animal density resulting in varying manure loading on the corral area.

## Conclusions

The quantification of NH<sub>3</sub> emissions from ground level area sources in a dairy is needed to understand which sources contribute most to the overall NH<sub>3</sub> emissions during winter and summer conditions. Summer and winter NH<sub>3</sub> emissions were estimated from an open-lot dairy.

Ammonia emission rate variations among GLAS occurred due to seasonal changes in ambient and source temperatures, and spatial variations of NH<sub>3</sub> occurred in the open-lot corrals due to varying cow density and the resulting dispirit manure (feces and urine) loading in feeding, dry and shaded area of the open lot. Within the open lot corral, summer NH<sub>3</sub> emissions from the dry area were significantly lower than those from shaded and feeding areas. While winter NH<sub>3</sub> emissions from feeding area were higher than shaded and dry areas, no statistically significant differences were detected in NH<sub>3</sub> emissions from the three divisions of the open-lot corral. Overall, summer NH<sub>3</sub> emissions were nearly twice those of winter emissions. It is necessary to consider both management practices and climate conditions to determine NH<sub>3</sub> emissions from the animal feeding operations.

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## The Agricultural Risks in Zone of Heavy Metal Pollution Point Source

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### Abstract

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

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

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

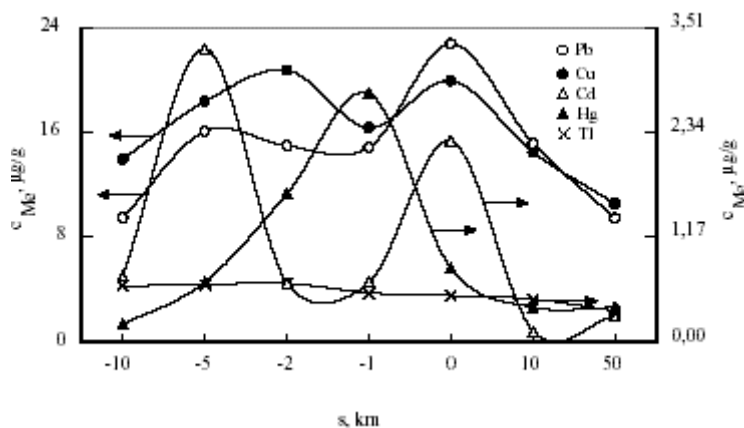
The acuity of the problem is due to the emplacement in the central zone of the country, densely populated (126 people/km<sup>2</sup>) and intensively used for agricultural food production, of a gigantic industrial complex, which includes two cement plants with total annual capacity of 4.4 million t/year,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

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

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

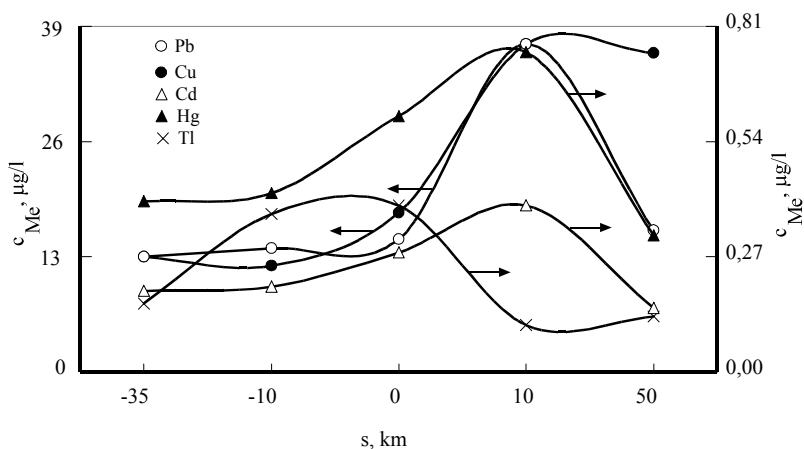
The content study of these toxic elements in water of the Dniester River, Dubasari reservoir (Figure 1) denote that in the proximity of the RRIC (zone with a radius of 10 km) the concentration of investigated heavy metals exceed 2-4 times the downstream level (50 km South). This fact attests that the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

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

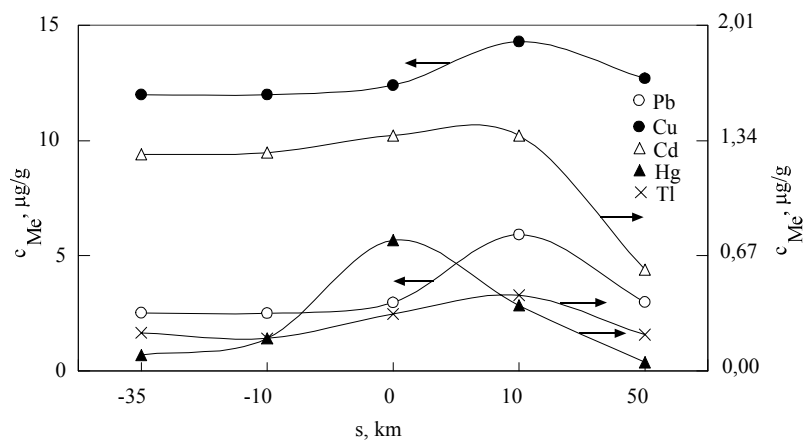


**Figure 2. Heavy metals content in adjacent soils of point pollution source zone**

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

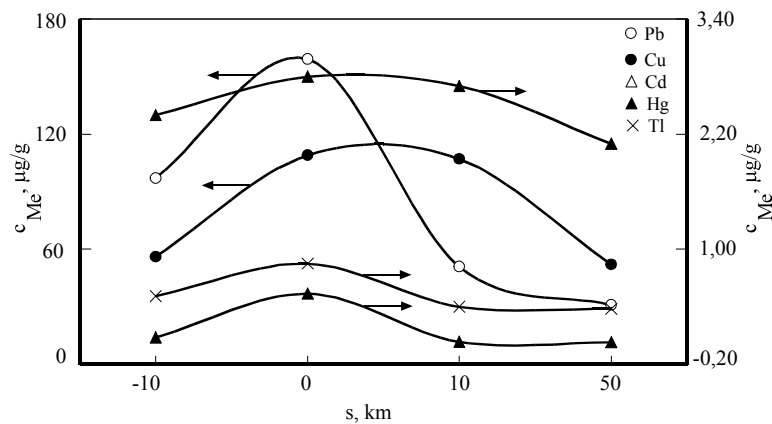


**Figure 1. Heavy metals content in water of Dubasari reservoir (Dniester River) in zone of point pollution source. Minus – northeast Rezina city, plus – Southeast.**



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

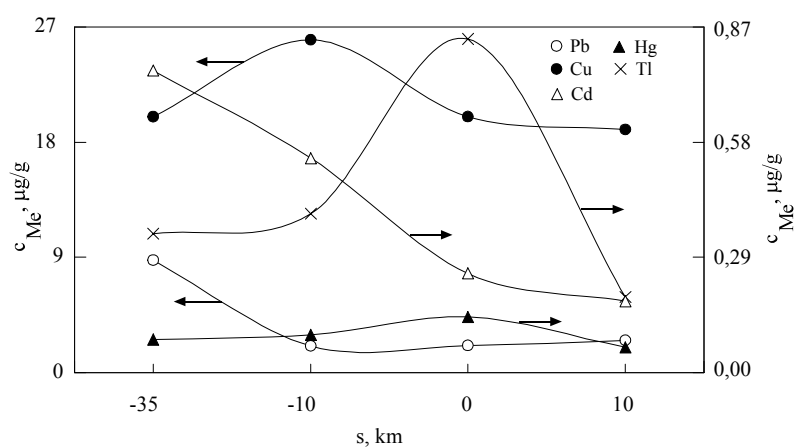
Determination of heavy metals content in freshwater vascular plants biomass (*Potamogeton perfoliatus L.*, *Butomus umbellatus L.*), which can serve as a model of intensively irrigated agricultural plants, demonstrate (Figure 4, 5) that these plants intrinsic absorb toxic elements from the environment,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



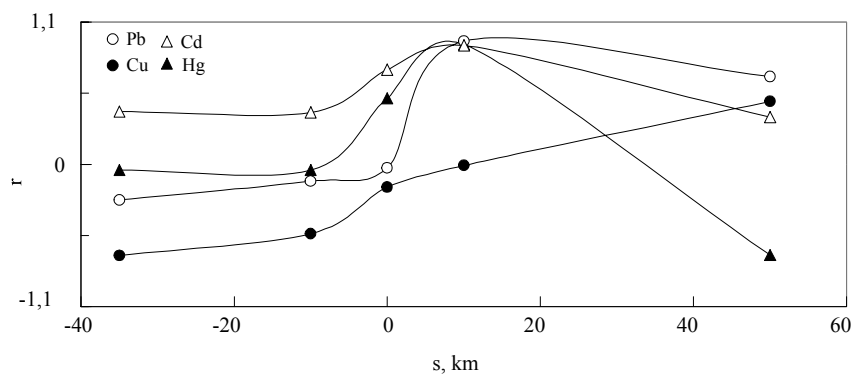
**Figure 3.** Heavy metals content in lichens *Xanthoria parietina* biomass in zone of point pollution source

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

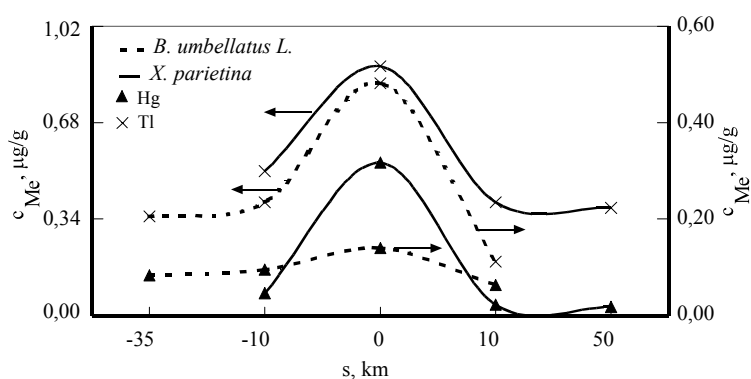
We have shown that considering the physiological properties of plants, some heavy metal can be assimilated directly from the atmosphere, facts confirmed by highly positive correlated linear dependence between the Tl and Hg contents in leaves of *Potamogeton perfoliatus* L., *Butomus umbellatus* L. and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



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



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



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

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