

## ABSTRACT

YAO, HAIYAN. Ammonia Emission from Stored Broiler Cake. (Under the direction of Dr. Sanjay B. Shah).

Ammonia emission from animal feeding operations has potential negative impacts on the environment and public health and it also reduces the nutrient value of animal waste. When conditions are not suitable for land application, broiler cake (or litter) may be stored in stockpiles which may contribute to ammonia emission. In this study, summer and winter ammonia emission factors from broiler cake stockpiles stored in a naturally ventilated shed were developed. The lab experiment measured relative ammonia emissions as affected by cover and depth of cake. Scrubbers were used to measure ammonia concentration both in the field and lab studies. In the field, the integrated horizontal flux (IHF) method and Fick's law of diffusion were used to determine ammonia emissions due to forced and natural convections, respectively. Ammonia emission due to natural convection was <0.01% of total emission. However, it may be necessary to calculate emissions based on concentrations measured only during conditions of forced convection. In summer, the estimated total ammonia-N loss was 0.8 % of total N. In winter, the total ammonia loss was 1.4 % of total N during the first 7 d and 2.5 % for the whole 15-d period. The estimated average daily ammonia emission factor in summer (7 d) was 24.5 g NH<sub>3</sub>-N/m<sup>3</sup>-d of cake or 7.0 g NH<sub>3</sub>-N/AU-d (AU = 500 kg LW). The estimated daily ammonia emission factor for the first 7 d in winter was 35.6 g NH<sub>3</sub>-N/m<sup>3</sup>-d or 42.5 g NH<sub>3</sub>-N/AU-d. The total ammonia lost during the 15-d winter study was 33.8 g NH<sub>3</sub>-N/m<sup>3</sup>-d or 40.2 g NH<sub>3</sub>-N/ AU-d. Ammonia losses from the tarp covered cake were significantly lower than the control and double depth treatments by 45% and 49%, respectively, at the end of study. Ammonia losses (g/m<sup>3</sup>) are lower from stockpiles with lower surface area per unit volume.

Ammonia Emission from Stored Broiler Cake

by  
Haiyan Yao

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APPROVED BY:

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Sanjay B. Shah, Chair

---

Jason A. Osborne

---

Dan H. Willits

---

Philip W. Westerman

---

Wayne P. Robarge

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Lingjuan Wang

## **BIOGRAPHY**

Haiyan Yao was born on 23rd February 1983 in Shijiazhuang city, Hebei province, China. After finishing the high school in Shijiazhuang No.2 Middle School she started her studies in the Department of Agricultural Structure & Bioenvironmental Engineering at China Agricultural University (CAU) in 2001. She received a degree of Bachelor of Science in Agricultural Structure & Bioenvironmental Engineering and a minor degree of Computer Science and Application from CAU in 2005. After graduation, she worked at a Real Estate Company for approximately 2 years in Beijing. Then she decided to pursue a master degree, and enrolled the Department of Biological and Agricultural Engineering at North Carolina State University (NCSU) in August 2007. During 2 y, she researched on ammonia emission from stored broiler cake under USDA National Research Initiative Grand. Finally, she got a Master of Science in Agricultural and Biological Engineering and a Minor in Statistics in 2009. After graduation, she decided to go back China and plan to apply what she learned to the related area.

Haiyan married Dr. Chaoyuan Wang in 2006.

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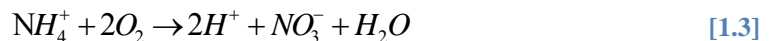
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incidences of respiratory diseases increase. Thus, high in-house ammonia concentrations can increase feed conversion, reduce animal growth, reduce carcass quality and increase mortality (Homidan *et al.*, 2003). When animal waste is land-applied as fertilizer, ammonia emission from animal waste can cause reduction in the nitrogen content of the waste, reducing its fertilizer value.

To protect workers' health, the U. S. Occupational Safety and Health Administration (OSHA) set a threshold ammonia concentration of 50 ppm for 8-h exposure (ATSDR, 2004). The American Conference of Industrial Hygienists set the threshold limit value (TLV) of time weighted average (TWA) concentration of 25 ppm for 8-10 h exposure and TWA short term exposure limit (STEL) of 35 ppm for 15-min exposure (ACIGH, 1999). When the ammonia concentration exceeds 300 ppm, it is dangerous to life or health (ATSDR, 2001).

Ammonia reacts with acidic compounds in the atmosphere to form extremely fine particulate matter (PM) or aerosols. These aerosols can reach the innermost parts of the lung and cause or enhance respiratory diseases (Alexander, 2009). When ammonia and ammonium are deposited on the soil, nitrification will occur, generating acid and may cause acidification of soils as shown in eq. [1.3] (Ni *et al.*, 1998).



Acidification of soil can increase dissolved metal concentrations in the soil that can adversely affect plant growth. Nitrogen as a fertilizer can increase crop productivity; however, over-fertilization caused by ammonia deposition may damage some sensitive crops such as tomatoes, cucumbers, conifers, and fruits when these crops are grown near ammonia sources (van der Eerden *et al.*, 1998). Enrichment of water bodies due to deposition or runoff by N (primarily as  $\text{NH}_3$  or  $\text{NH}_4^+$ ) may cause algal blooms in surface waters, resulting in eutrophication. Eutrophication may cause the decline in aquatic species and thus reduce the economic and recreational value of water bodies. Because

ammonia may cause environmental, ecological and quality of life (odor) problems, its emission has caused concerns among the public, scientists, and policy makers.

### 1.3 Regulating livestock air emissions

In the US, in the late 1990s, the EPA began to realize that there was not sufficient air emissions data to regulate animal feeding operations (AFOs) under the Clean Air Act (CAA), the main air quality regulation in the US. In 2001, to solve this problem, the EPA began discussions with AFO owners (EPA, 2006). The EPA announced an Air Quality Compliance (AQC) Agreement with AFOs on Jan. 21, 2005 (EPA, 2005) to ensure that AFOs complied with existing air quality regulations. Under this agreement, cooperating AFOs agreed to participate in a nationwide project to measure the air emissions from AFOs and then help to develop an effective regulatory program. Hence, emissions from houses, storage and treatment facilities may be regulated in the future.

As part of the AQC agreement, the EPA developed a monitoring program NAEMS (National Air Emissions Monitoring Study) headed by Purdue University to monitor emissions and develop standard methodologies for estimating these emissions. The air pollutants selected for monitoring include NH<sub>3</sub>, hydrogen sulfide (H<sub>2</sub>S), total suspended particulates (TSP), particulate matter (PM<sub>10</sub>, PM<sub>2.5</sub>) and volatile organic compounds (VOCs) (NAEMS, 2008). As of 2009, the EPA is monitoring air emissions from poultry, dairy and swine AFOs in nine states as part of the two-year study. North Carolina State University is also involved in the NAEMS study to measure emissions from layer and hog facilities. The results of the NAMES monitoring study as well as other published and ongoing studies will be used to develop emission factors [i.e., kg/AU-d, where AU (Animal Unit) = 500 kg live animal weight].

Another federal air quality regulation that can impact AFOs is the Environmental Planning and Community Right-to-Know Act (EPCRA). As required under section 304 of EPCRA, AFOs are

required to report daily emissions of NH<sub>3</sub> and H<sub>2</sub>S exceeding 45.4 kg (100 lb/d). However, the requirement to report releases of ammonia and H<sub>2</sub>S from animal farms under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) was cancelled ([Federal Register, 2008](#)).

The EPA Concentrated Animal Feeding Operations (CAFO) final rule also stipulates that animal waste stockpiled outside for more than 15 d should be covered. Since the EPA may regulate emissions from animal waste stockpiles under CAA, there is a need to develop emission factors from different waste storage methods (cover vs. no cover). While there have been many studies on monitoring ammonia emission from animal houses, there are only a few studies on monitoring emissions from stockpiles. Hence, more studies on monitoring broiler litter stockpiles emissions are required for developing emission factors even when other published and ongoing studies are taken into account because many factors, such as, season, diet, and storage type affect emissions.

However, as recommended by the National Research Council (NRC), a process based model is required (NRC, 2003) that can simulate emissions from waste stockpiles for a wide range of waste properties, weather conditions, and storage conditions. Data collected from field studies such as the one proposed here could then be used to test the predictive power of such a model.

## **1.4 Research objectives**

The overall objective of this research was to measure ammonia emission from stored broiler cake as affected by season, cover type, and depth of storage. Specific objectives were to:

- 1) develop ammonia emission factors from broiler cake stockpiles stored in a litter shed as impacted by season (summer and winter); and
- 2) evaluate the impact of cover (uncovered vs. covered with tarpaulin) and stockpile depth (control depth vs. double the control depth) on ammonia emission.

Ammonia emission factors mentioned in specific objective 1 can be expressed in different ways. It can be expressed as flux, i.e., mass emitted per unit surface area per unit time ( $\frac{kg}{m^2 - d}$ ). Ammonia emission factor can also be expressed in terms of mass of cake ( $\frac{kg}{Mg - d}$ ), volume of cake ( $\frac{kg}{m^3 - d}$ ), and per animal unit (AU= 500 kg) basis ( $\frac{kg}{AU - d}$ ). Ammonia-N emission can also be expressed as percent of total N in the broiler cake stockpile. The purpose of specific objective 2 was to compare relative ammonia emissions from three different treatments applied to chambers in the laboratory.

The broiler cake used in this study is somewhat different from broiler litter. Broiler litter refers to the mixture of bedding, feces, spilled feed and water, and feathers on the floor of a broiler house while broiler cake is predominantly fecal material and spilled feed (and water) that accumulates under feeders and waterers. Whereas broiler litter is completely removed after a number of grow-outs to be replaced with fresh bedding material, broiler cake is removed from the house after each grow-out.

## 2 LITERATURE REVIEW

In this chapter, the techniques for measuring ammonia concentration and flux are reviewed. Factors that affect ammonia emissions are discussed. Research on ammonia emission from solid animal waste and broiler litter stockpiles are also reviewed.

### 2.1 Measurement of ammonia concentration

Many methods have been developed for measuring ammonia concentrations. These can be classified as: acid neutralization, detector tube, spectroscopy, electrochemical sensor, color intensity system, and solid-state sensors (Ni *et al.*, 2008).

#### 2.1.1 Acid neutralization

##### **Acid trap, impinger or scrubber**

This method is based on the neutralization of the base ammonia by acid. When air passes through an acid solution, ammonia in the air will convert to  $\text{NH}_4^+$  immediately. Then the  $\text{NH}_4^+$  concentration in the scrubber can be determined in the lab by electrode, colorimetry, photometry, conductimetry, or titrimetry (Shah *et al.*, 2006; Valentine, 1964; Valli, 1991; Ni *et al.*, 2008). Ammonia concentration in the air is then calculated based on the air flow rate, the duration of deployment, solution volume, and the concentration of the  $\text{NH}_4^+$  in the solution.

This method has high trapping efficiency (>97%) (Shah *et al.*, 2006), is simple and is moderate in cost. However, it cannot separate the particulate  $\text{NH}_4^+$  from the gas, needs more labor than the other methods (such as spectroscopy) and can only provide time weighted average concentrations. When the operation time is more than 24 h, the loss of acid volume can reduce trapping efficiency. Condensation in the tubing and salt precipitation in the scrubber are also concerns.

## **Filter pack**

A filter pack typically contains an acid coated filter paper placed downwind of an uncoated filter paper. The uncoated filter traps particulates and the ammonia in the air is then trapped by the acid coated filter. After the experiment, the filter is eluted and analyzed for ammonium. Citric acid, oxalic acid, tartaric acid, and sulfuric acid are often used for coating the filter and the performances of the different acids are comparable (Rabaud *et al.*, 2001). The detection limit for the filter pack is 0.2-2.8 µg/filter (Shah *et al.*, 2006).

Filter packs can separate the ammonia aerosols and gas. However, depending upon the temperature and humidity, the aerosols can dissociate and ammonia can pass through the uncoated filter. This may result in overestimation of the ammonia concentration (Shah *et al.*, 2006). Further, the operation time should be controlled carefully to prevent saturation (Andersen and Hovmand, 1994). Contamination of the filter pack during preparation is also a concern.

## **Denuder**

The denuder generally consists of a tube coated with an acidic medium on the inside. Since gas and aerosol have different diffusion velocities, it can separate the gas form from aerosol. As the air passes through the tube, ammonia will be absorbed by the acid coating (citric acid, oxalic or phosphorous acid medium). The acid medium is then eluted for lab analysis.

The annular denuder has two concentric acid coated tubes and air passes though the annulus (Shah *et al.*, 2006). It has more contact surface than the simple denuder. So it has higher detection limit than a simple denuder (Allegrini *et al.*, 1994).

Denuders can be forced-air and passive in design. The forced-air denuder receives air from a pump while the passive denuder requires no forced air. The advantage of the passive denuder is that it

can measure the ammonia flux in the absence of measured wind speed, but it needs to be calibrated in the wind tunnel. Further, compared to the forced denuder, the passive denuder costs less and can provide flow-weighted concentration data (Shah *et al.*, 2006). When real-time concentration is not required, the passive denuder is preferred to forced-air denuder (Shah *et al.*, 2006). Phillips *et al.* (2001) reported that the passive denuder (flux sampler) was widely used for ammonia flux measurement from non-point sources like land spreading, but it was less widely used for manure heaps, slurry stores and animal buildings.

### 2.1.2 Detector tube

The detector tube is a scaled glass tube containing a chemical. When air passes through the tube, the gas of interest reacts with the chemical and changes the color of the tube. The length of color indicates the concentration of the gas in the air. It can measure ammonia concentration above 1 ppm (Dräger, 1997). The accuracy reported by Liu *et al.* (1993) was  $\pm 1$  ppm. The detector tube is not suitable at low concentrations because the accuracy and precision degrade as concentration decrease (Ni *et al.*, 2008). There are two types of tubes: active tubes and passive tubes. An active tube requires a hand pump to pull air through the tube. The active tube has short measuring times of 10 s to 15 min (Phillips *et al.*, 2001). In a passive tube, air enters the tube through diffusion. The measuring time for passive tubes is several hours. Detector tubes are used mostly for management because they lack the accuracy required for research studies.

### 2.1.3 Spectroscopy

#### **Fourier transform infrared spectroscopy (FTIR)**

This system consists of an interferometer (fixed mirror and moving mirror), detector, light source and the beam splitter. The interferometer is used to produce the interferogram as an output signal. After the movable mirror is displaced, it produces some chemical structure information based on

vibrational modes. Each vibrational mode can provide a specific absorption spectrum, which is like a fingerprint. When the spectrum (fingerprint) is determined, the gas and its concentration can be determined based on a reference spectrum (gas of known concentration) (Ni *et al.*, 2008). A reading can be obtained every minute or even every few seconds. For ammonia, the detection limit is 1.5 ppb (Biermann *et al.*, 1988). However, this system needs an experienced operator and the cost is high. Another drawback is that it needs careful and frequent calibration (Phillips *et al.*, 2000).

### **Non-dispersive infrared analyzer (NDIR)**

The NDIR consists of a lamp as an infrared (IR) source, a chamber, a wavelength filter and a detector. It measures the spectral absorption of a gas at one spectral band of the IR spectrum (Phillips *et al.*, 2000). As thermal background signal will affect the results, the IR signal is usually modulated (chopped). It also needs correction for temperature and pressure (Phillips *et al.*, 2000). The photoacoustic spectrophotometer (PAS) is based on NDIR which determines gas concentration based on pressure changes resulting from temperature changes. For ammonia, the NDIR has a detection limit of ~0.2 ppm (Phillips *et al.*, 2000).

### **Ultraviolet differential optical absorption spectroscopy (UV-DOAS)**

This method uses a xenon lamp as a light source. It is similar to the IR analyzer but the measurements are made in the ultraviolet (UV) region. The absorption coefficients in UV are higher than in IR. However, as UV-DOAS uses a narrow light source, in field studies, it is difficult to collimate the transmitter and receiver (Klarenbeek *et al.*, 1993). Mennen *et al.* (1996) reported that the noise level of this system was 3 ppm, which was too high for many agricultural applications. Further, the cost of the UV-DOAS is high.

## Chemiluminescence analyzer

Chemiluminescence analyzers are based on a two-step process. The first step involves conversion of ammonia to nitric oxide (NO). The resulting NO is then analyzed by chemiluminescence. The sensitivity of this method is 1 ppb and the precision is  $\pm 0.5$  ppb (Ni *et al.*, 2008).

In general, spectroscopic methods are accurate, have low detection limits, and provide real-time data. However, they are expensive, require regular maintenance and calibration, and require a power source.

### 2.1.4 Electrochemical sensor

Instrumentation using electrochemical detectors usually require that ammonia gas be captured by a combination of electrochemically active reagents. The ammonia concentration is related to the electric potential or current generated due to the reaction (Phillips *et al.*, 2001). Phillips *et al.* (2001) reported that electrochemical sensors for ammonia had a minimum detection limit (MDL) of 5 ppm though newer electrochemical sensors have MDLs of 1 ppm (e.g., Dräger XSNH<sub>3</sub>). Because electrochemical sensors have short response times, they can be used as toxic gas monitors in alarm systems (Phillips *et al.*, 2001). The disadvantage of this sensor is that many other gases can affect its response and its sensitivity changes when exposed to ammonia for long time (Phillips *et al.*, 2001). The most common reported sensor of this type is the Dräger sensor which has been used to monitor ammonia concentrations in pig, broiler, and turkey houses (Ni *et al.*, 2008).

### 2.1.5 Color intensity system

This system is based on the colorimetric principle. It has a porous paper coated with a chemical. When the tape is exposed to the sample gas, it changes color. The color intensity is based on the gas concentration. Based on the tape type, this system can measure concentrations of different gases. The

low-level ammonia detection Chemcassette<sup>®</sup> tape has a range of 0.5-30 ppm and the response time is just a few seconds. (Ni *et al.*, 2008).

### 2.1.6 Solid-state sensor

Solid-state sensors are also called electronic sensors and many are still under development. The advantage of this type of sensor is that it is simple, has a quick response and is low-cost. The disadvantage is its low accuracy and drift (Ni *et al.*, 2008). It is also affected by humidity and other gases. One solid sensor tested by Berckmans *et al.* (1994) in livestock buildings had a detection range of 0-100 ppm and response time was 10-15 s for ammonia.

## 2.2 Measurement of ammonia emission

There are three methods for measuring ammonia emission: enclosures, N recovery, and micrometeorological methods (Shah *et al.*, 2006). These methods are discussed below.

### 2.2.1 Enclosure method

In the enclosure method, the NH<sub>3</sub> released from the treated surface is confined. This method can be closed-static, semi-open, or closed-dynamic in design (Shah *et al.*, 2006). While dynamic chambers have air exchange, static chambers do not have air exchange. In the closed-static and semi-open chamber, the flux of ammonia is determined by the mass of ammonia recovered on the trapping medium and the area of the emission surface. In the dynamic chamber, the flux is determined based on the difference in concentration of the ammonia at the inlet and outlet, air flow rate, duration, and the treated emission surface area. The wind tunnel is also an example of the dynamic chamber.

The enclosure method is not suitable for developing ammonia emission factors because it modifies the internal environment (Shah *et al.*, 2006). However, enclosures can be used for comparing relative emissions (Shah *et al.*, 2006). The closed-dynamic chambers are preferable over the other two enclosure types because they can better mimic natural conditions (Shah *et al.*, 2006).

### 2.2.2 Nitrogen recovery

The Nitrogen (N) recovery method requires an N mass balance. After quantifying the amounts of N at the beginning and end of the test period, gaseous N loss from the system can be calculated as the difference. When using N recovery method to measure ammonia flux, it is commonly assumed that the entire gaseous N lost is as ammonia. Because ammonia volatilization and denitrification can happen simultaneously, such an assumption may result in overestimation of N loss since ammonia flux only represents a part of the total gaseous N lost. It may also introduce large errors due to uncertainties in quantifying the N addition and loss terms (Shah *et al.*, 2006). So the N recovery method is not suitable for measuring ammonia emission.

### 2.2.3 Micrometeorological method

There are four micrometeorological methods used for measuring gas flux: eddy correlation, gradient diffusion, integrated horizontal flux (IHF) or mass balance, and backward Lagrangian stochastic (bLS) model (Shah *et al.*, 2006). The main advantage of a micrometeorological method is that it has minimal effect on the environment and hence, its results are representative of natural conditions. It can also measure the average flux over a large area and thus reduce the impact of non-uniform emissions. It is difficult to replicate micrometeorological studies because of large plot sizes and separation distances.

#### Eddy correlation

The vertical flux of a gas is calculated (Denmead, 1983) as:

$$\Phi = \overline{wC_g} + \overline{w'C'_g} \quad [2.1]$$

where  $\Phi$  (mg/m<sup>2</sup>-s) is the gas flux,  $w$  (m/s) is vertical wind speed, and  $C_g$  (mg/m<sup>3</sup>) is the gas concentration,  $\overline{wC_g}$  denotes mean values, and the term  $\overline{w'C'_g}$  denotes the fluctuations from the mean. This method is based on the assumption that the mean vertical wind speed  $\bar{w}$  is equal to zero

over a uniform flat surface. So based on this assumption, the ammonia flux is equal to the fluctuation  $(\overline{w'C'_g})$ .

The disadvantage of the eddy correlation method is that it requires an appropriately fast detector, because in the natural environment, eddies occur with frequencies extending up to 5 or 10 Hz (Denmead, 1983).

### **Gradient diffusion**

The equation for gradient diffusion (Denmead, 1983) is:

$$\Phi = -K_g \frac{\partial \overline{C_g}}{\partial z} \quad [2.2]$$

where  $K_g$  ( $m^2/s$ ) is eddy diffusivity and  $z$  (m) is measurement in the vertical plane. The term  $K_g$  can be determined by the equation (Denmead, 1983):

$$K_g = \frac{ku_*z}{\varphi_g} \quad [2.3]$$

where  $k$  is von Karman constant (0.41),  $u_*$  (m/s) is friction velocity parallel to the surface and  $\varphi_g$  is the stability function (dimensionless).

The aerodynamic method and energy balance method are based on the gradient diffusion principle. The aerodynamic method is not suitable for very rough surfaces (i.e. forests) while the energy balance method is not suitable for measurement at night (Shah *et al.*, 2006). Like eddy correlation, the gradient diffusion method requires a large homogeneous surface.

### **Integrated horizontal flux**

The integrated horizontal flux (IHF) method is also called the mass balance method. The IHF method is based on the principle that the target gas emitted (vertically) from the treated surface of unit

width and then, transported horizontally, is captured in a vertical plane of the same width downwind.

The gas flux is calculated (Denmead, 1983) as:

$$\Phi = \frac{1}{x} \left[ \int_{z_0}^{z_p} (\overline{uC_g})_e dz - \int_{z_0}^{z_p} (\overline{uC_g})_b dz \right] \quad [2.4]$$

where x (m) is the fetch (distance upstream of the measurement that is relatively uniform); u (m/s) is the horizontal wind speed;  $C_g$  (mg/m<sup>3</sup>) is the gas concentration;  $\overline{uC_g}$  (mg/m<sup>2</sup>-s) is the time averaged total gas flux in the horizontal direction;  $z_0$  (m) is the roughness length; and  $z_p$  (m) is the height of the profile development. The subscripts e and b apply to the experimental and the background emissions, respectively.

The ZINST method is a special case of the IHF method. In this method, gas concentration and wind speed are measured at a single height to determine the gas flux. The ZINST method requires a flat uniform area (Shah *et al.*, 2006). So it is not suitable for measuring ammonia emission from a litter stockpile.

### Backward Lagrangian stochastic (bLS) model

Based on the concentration of a gas measured at a certain height within or downwind of the source area, the backward Lagrangian Stochastic (bLS) model calculates the trajectories of the gas molecules, thereby, modeling emissions from the source area (Flesch *et al.*, 1995). The flux is calculated based on horizontal wind speed, gas concentration and wind direction as (Flesch *et al.*, 1995):

$$\Phi = \frac{\overline{C_g}(z_m)\overline{u}(z_m)}{n} \quad [2.5]$$

where  $C_g$  is concentration at height  $z_m$ ;  $z_m$  is the height of the source (tower), u is the wind speed and

$$n = f(z_m, z_0, L, h, G) \quad [2.6]$$

where L is the Obukhov stability length, h is the depth of mixed layer, and G is source characteristics. Ten- to 30-min time averaged data is the most appropriate for this model (Shah *et al.*, 2006). This model requires gas concentration measurement at a single height and is suitable for smaller areas; however, it is not suitable for stable conditions and transient periods in stratification (Shah *et al.*, 2006).

### 2.3 Summary

To develop ammonia emission factors from waste stockpiles, it is not necessary to separate the gas and aerosol fractions. Spectroscopic methods, electrochemical sensor, or chemcassette detection system would be very expensive for measuring emissions from stockpiles because simultaneous measurements are required at multiple heights. Further, at each height multiple conditions (e.g., forced vs. natural convection) may need to be evaluated. For time weighted average measurements, using the acid scrubber, which is relatively inexpensive and efficient (97% efficiency) is a viable option. Using inexpensive solenoid switches to direct air to a particular scrubber for a specific condition is quite feasible. As the broiler cake stockpile does not have a large homogeneous surface, the eddy correlation and gradient diffusion method are not suitable for measuring ammonia flux in this study. Because the bLS model is not suitable for stable conditions, it may not be suitable for measuring ammonia emission under natural convection (or natural convection, which is based on the molecular diffusion) inside storage sheds. Hence, the IHF method is probably the most suitable method to measure ammonia flux from broiler cake stockpiles.

## 2.4 Factors affecting ammonia generation in waste

There are many factors that affect the release of ammonia: temperature, pH, moisture content, carbon/nitrogen ratio, and oxygen level. To better measure, understand, and control ammonia emissions, it is important to understand the effect of these factors on  $\text{NH}_3$  generation.

### Temperature

As gas solubility decreases with increasing temperature, ammonia emission increases with temperature of the waste. Also with increase in temperature up to a certain point, microbial and enzymatic activities increase resulting in increased ammonia production. Air temperature may also affect convective mass transfer coefficient (Liu *et al.*, 2007) while waste temperature may affect the dissociation constant ( $\text{NH}_3$  vs.  $\text{NH}_4^+$ ), diffusion, and generation of ammonia in waste (Liu *et al.*, 2007).

### pH

The pH of waste plays an important role in ammonia volatilization because the ratio of  $\text{NH}_3$  to  $\text{NH}_4^+$  depends on the pH of the waste. When pH is below 7, the rate of ammonia release is very small (Reece *et al.*, 1985). With increasing pH, ammonia concentration increases. When litter pH decreased, enzymatic and microbial activities decreased (Weaver and Meijerhof, 1991). Ivanoy (2001) found that ammonifying bacteria were inhibited when  $\text{pH} < 6$ . In litter, uric acid decomposition is mostly happens under alkaline conditions ( $\text{pH} > 7$ ) (Blaker and Hess, 2001). Uricase which catalyzes uric acid breakdown, is most effective at a pH of 9 (Blaker and Hess, 2001). Hence, inhibition of bacterial and enzymatic activities due to reduced pH may further decrease ammonia generation.

### Moisture content

Ammonia generation in waste results from the enzymatic and microbial activities. Carey *et al.* (2004) found that microbial breakdown of uric acid increased with moisture in litter. Sims and Wolf

(1994) reported that the conversion rate of uric acid to ammonium-N could be affected by moisture content. Ferguson *et al.* (1998) reported that ammonia release increased with litter moisture content. Elliott and Collins (1982) reported the wet litter led to high ammonia levels in broiler houses. Liu *et al.* (2007) found that when water was added to the litter, ammonia emission was suppressed for a short time but rebounded after 1-2 weeks. However, under very wet conditions, scarcity of O<sub>2</sub> will slow down the enzymatic and microbial activities. Decrease in ammonia concentration at very high moisture level has been reported in many studies (Valentine, 1964; Schefferle, 1965; Carr *et al.*, 1990; and Liu *et al.*, 2007).

### **Carbon/nitrogen ratio (C/N ratio)**

Ammonia generation depends on the total ammoniacal nitrogen (TAN= NH<sub>3</sub>-N + NH<sub>4</sub><sup>+</sup>-N) in the litter (Liu *et al.*, 2007). Carbon is essential for cell material synthesis and energy, and nitrogen is essential for building cell proteins. So if litter contains more carbon-rich organic materials, more ammonium can be immobilized. The extent of N immobilization depends on the carbon content of the litter (Jeppson, 1999). Hence increased N immobilization will result in reduced ammonia release from the litter. Poincelot (1974) found that if C/N ratio was <26, more N was lost as ammonia to the atmosphere than when C/N was >26. Kirchmann (1985) found that if the C/N ratio was more than 50, ammonia N loss was negligible.

### **Oxygen level**

Scarcity of O<sub>2</sub> will slow down enzymatic and microbial activities, which will slow down ammonia generation. Since Groenestein and van Faassen (1996) found that oxygen content decreased with increasing depth in the litter, more ammonia emission may occur from the surface layer of the litter than deep within the stockpile.

## 2.5 Ammonia emissions from stored solid animal waste

More studies have been carried out on monitoring ammonia emissions from broiler houses in different countries than on monitoring ammonia emissions from litter stockpiles. Selected studies on ammonia emission from stored animal waste, with emphasis on broiler waste are reviewed below.

*Sagoo et al.* (2007) measured ammonia emission from broiler litter with wind tunnels for 6 months in the UK. The manure heaps (15 m<sup>3</sup>, ca 5-6 Mg fresh weight) were stored in 'bunkers' with concrete blocks (0.5 m high) on three sides and the fourth side had straw bales (lined with polythene). The entire manure heap was enclosed and vented by a wind tunnel. An acid scrubber was used to determine ammonia concentration and NH<sub>3</sub> emission was calculated based on the measured concentration and calculated airflow rate. Measurements were made immediately, after 3, 7, 14, 21, and 28 d and then at monthly intervals from five different treatments. The treatments were conventional (open air), sheeted (plastic cover), turned-twice (turned after 2 weeks and 2 months in open air), 'A-shaped' (open air) and roofed (covered building). The highest emission came from roofed heaps (19% of initial N) while the lowest emission came from the sheeted heap (1.3% of initial N). The A-shaped, conventional and turned treatments lost 12.9, 13.2, and 15.6% of initial N, respectively.

*Liu et al.* (2007) measured ammonia emissions as affected by moisture content of broiler litter placed in a dynamic flow-through chamber. They concluded that higher moisture content resulted in higher ammonia emissions. With very high moisture content (>35.1%), ammonia emissions decreased for >6 d. Further, older litter (4 yr) resulted in higher ammonia emission than newer litter (1 yr) by 370%.

*Tasistro et al.* (2007) studied NH<sub>3</sub> emissions from five bedding materials (mixed with broiler manure) and the effect of PLT<sup>TM</sup> (an acidifier) on ammonia emission from broiler manure. The five

bedding materials and two acidification levels (control and PLT™) were combined in a complete factorial arrangement with three replications. The treatments were applied to cylinders that were incubated at 25°C with 98% humidity for 11 d. Ammonia was trapped in scrubbers and measured colorimetrically as  $\text{NH}_4^+$ . The flow rate through the incubation chamber was 0.07 L/min. They reported that total ammonia emissions from peanut hulls and shredded paper were the highest (vs. wood shavings, sawdust, and wheat straw) and ammonia emission was inhibited by PLT™ throughout the 11-d study. There were no significant interactions on ammonia emissions between PLT™ and bedding materials.

[Wang et al. \(2006\)](#) investigated ammonia emission from broiler litter in a dynamic flow-through chamber (50 L, flow rate of 9.8 L/min) using different ammonia measurement methods (chemiluminescence, acid scrubbers and N balance method). They reported that ammonia emissions were very sensitive to litter moisture content. The N mass balance method estimated the highest ammonia emission while the scrubber estimated the lowest emission.

[Zemek et al. \(2005\)](#) measured ammonia emission from broiler and pig waste storage piles placed in enclosures using photoacoustic sensors in the Czech Republic. The waste samples were treated with the biotechnological agent Amalgerol. Ammonia emission rates from treated and untreated broiler storage piles surface were 1.89 g/h-m<sup>2</sup> and 3.20 g/h-m<sup>2</sup>, respectively. Ammonia emission rates from the treated and untreated pig storage piles surface were 3.61 g/h-m<sup>2</sup> and 5.63 g/h-m<sup>2</sup>, respectively. The agent significantly reduced ammonia emissions by 41.2% and 35.9% from the broiler and pig waste storage piles, respectively.

[Nicholson et al. \(2004\)](#) measured ammonia emissions from broiler litter and laying hen manure in four experiments: 1) broiler litter types and quantities, 2) broiler drinker design (affecting litter moisture content), 3) laying hen manure removal frequency, and 4) different laying hen housing

systems (belt-scraped, deep-pit and stilt house) in the UK. A large walled trailer was used to store the waste heaps (experiments 1-3). Masts were erected on each wall and pairs of passive denuders (Ferm *et al.*, 1991) were attached on the masts at three heights (0.2, 0.5 and 1.0 m for experiments 1-3 and 0.2, 0.8, 2 m for experiment 4). Broiler litter (2 Mg/heap) was stored for 6-12 months (experiment 1 & 2). For experiment 3, four layer manure heaps (6-8 Mg/heap) were stored for 10-16 month. For experiment 4, eight layer manure heaps (2 Mg/heap) were stored for 5 months. The denuders were changed at 2-8 week intervals throughout the 5-16 month storage period. There were no differences in ammonia emissions between different litter types/rates or drinker treatments during broiler litter storage with ammonia losses ranging from 42 to 572 gNH<sub>3</sub>-N/m<sup>2</sup> of initial heap surface area (experiments 1 & 2). The total N content declined 45-60% during storage for experiment 1 & 2. For experiment 3, the total NH<sub>3</sub>-N loss was 508-1,111 g/m<sup>2</sup> initial heap surface area. For experiment 4, the total NH<sub>3</sub>-N loss for stilt, deep-pit and belt-scraped manure were similar (560-764 g/m<sup>2</sup> initial heap surface area). The N content of manure declined by 19-43% during storage in experiment 4.

Sommer *et al.* (2004) measured ammonia concentrations over cattle manure stockpile (cone shape, with base diameter 3.1 m, top surface diameter 0.5 m, and height 1.1 m) in Canada. Ammonia emissions were measured with the IHF and bLS methods. For the IHF method, the passive flux (shuttle) samplers were mounted on the two sides of a rotating arm at five heights (0.44-2.4 m) on the downwind side and at three heights (0.44-2.4 m) on the upwind side. For the bLS method, the line concentration was measured with open path laser at 1 m height and 1.7-3.6 m from the source while the background fluxes was measured with passive flux sampler at 2.4 m. Ammonia emission was measured for 19 d. The two methods gave similar mean ammonia emission estimates and similar emission patterns. Based on IHF method, ammonia emission accounted for 3.4% of the initial total-N during a 7-d period.

Rodhe *et al.* (2002) compared ammonia emission from two rectangular broiler manure stockpiles (covered with straw & uncovered) using passive flux samplers at four heights (0.46-8.00 m) at four points along the perimeter in Sweden. The IHF method was used to measure ammonia emission. Cumulative ammonia loss from the uncovered heap was 7% of total N while it was 10% of total N from the covered heap.

Petersen *et al.* (1998) measured ammonia emission from solid pig and cattle manures with paired tube denuders at four heights (0.25-2.5 m) at four points placed along the circumference of circular stockpiles in Denmark. The IHF method was used to measure ammonia emission. There was little difference in cumulative ammonia loss between seasons for both manures, but there were distinct differences between manure types. The losses of ammonia from cattle manure were 4-5% of total N while the losses from pig manure were 23-24% of total N.

Although some work has been done on monitoring ammonia emission rates from broiler litter stockpiles, there is need for additional data to determine seasonal ammonia emission factors from broiler litter or cake stockpiles. Based on the review of published studies presented above, the IHF method was the most frequently used method for monitoring ammonia emission from stockpiles.

Further, no studies that evaluated ammonia emissions based on both forced and natural (free) convections could be located in the literature. If the stockpile is stored under a shed with covered sidewalls (as is customary of litter sheds in NC), it would seem reasonable to assume that under low wind conditions or when wind blows against the sidewall, natural convection could be an important mechanism for ammonia emission. Hence, there is also need to evaluate the contribution of natural convection to total ammonia emission.

Since North Carolina regulations require poultry litter to be covered if stockpiled outside for >15 d, many poultry producers cover stockpiles. Covering a stockpile will affect both water and air

qualities. Sagoo *et al.* (2007) was the only study on tarp covered stockpiles and it showed that covering significantly reduced ammonia loss from broiler manure. Hence, confirming the air quality benefits by covering a stockpile in a follow-up study seems reasonable. Further, the shape of the stockpile, i.e., surface area to volume ratio may also play an important role in ammonia emission; however, no studies that evaluated the impact of stockpile shape could be located in the literature. While ammonia emission comparisons from stockpiles based on cover and shape would be most useful if conducted at the field scale, it is difficult to conduct such a study at the field scale due to space considerations as well as confounding effects. Hence, an experiment conducted with the treatments applied to chambers could still be useful to compare relative emissions as impacted by cover and shape of stockpile.

### 3 MATERIALS AND METHOD

#### 3.1 Research site

The field study was conducted on a broiler farm in Tar Heel, NC, which is ~150 km south of North Carolina State University (NCSU), Raleigh. There are four broiler houses on the farm. Each house can hold 20,700 chicks that are raised on litter for 60-63 d. The litter shed (Figure 3-1) is 26 m in length, 13 m in width, and 4.4 m in height at the ridge line. It is located at the southeast corner of the farm. A mature tree line borders the shed on the east and south.

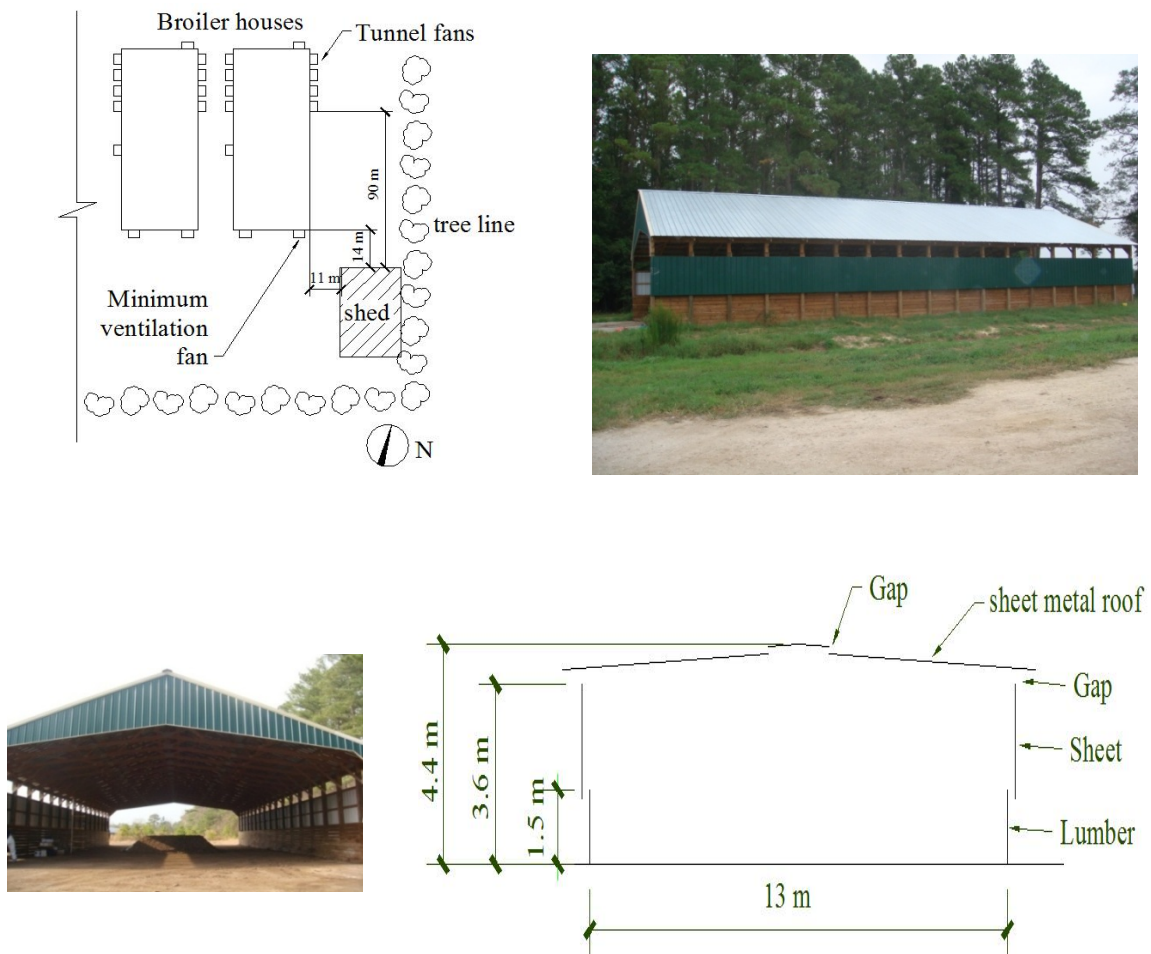


Figure 3-1 Location of the litter shed and its pictorial and schematic presentations

## 3.2 Field study

Ammonia emissions were measured from broiler cake stockpiles in summer 2008 and winter 2009. Ammonia emissions from the summer stockpile were monitored for 9 consecutive days and from the winter stockpile for 15 consecutive days. Details are provided below.

### 3.2.1 Stockpile construction

In both summer and winter, the broiler cake was transported from the broiler house to the litter shed using a tractor-drawn decaker/cruster. The stockpile was built using a front-end loader. In winter, the mass of the cake (15,550 kg, wet base) was determined by weighing every load applied to the stockpile. In summer, the mass of the stockpile was estimated to be ~ 15,900 kg (wet base) based on the moisture content, volume, and bulk density of the cake in winter stockpile. The stockpile was shaped like a trapezium. The dimensions of the stockpiles in summer and winter were similar. The stockpile base was ~6.5 m in length, ~4.7 m in width and ~0.9 m in height (summer). In winter, the stockpile height was ~1.1 m. At the top, the stockpile was ~5.5 m in length and ~4 m in width (Figure 3-2). Both in summer and in winter, the stockpile was located approximately at the center of the shed.

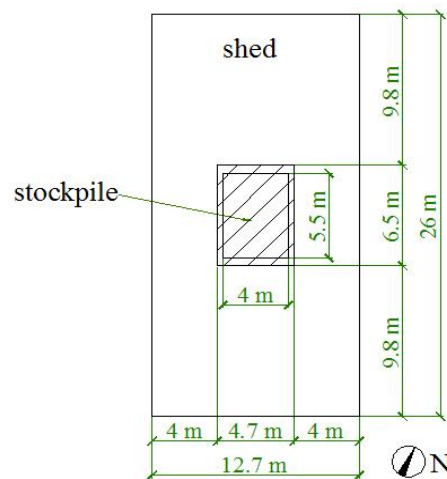


Figure 3-2 Approximate location of the stockpile in the litter shed

In both summer and winter, the stockpile was located approximately at the center of the shed (Figure 3-2) to minimize turbulent wind effects over the stockpile surface. The small size and

relatively low height of the stockpile (in relation to the shed dimensions) were also selected to minimize turbulence. It was recognized that a producer would have built a much larger stockpile that would have spanned the entire width and most of length of the shed. While a larger stockpile would have yielded more representative emissions, it was felt that stockpile portions closer to the sidewalls would not experience the same wind profiles as the central portion due to edge effects.

In summer, the stockpile was built on Aug. 8, 2008. However since there was additional cake in the shed at that time, the stockpile was covered with a tarpaulin to prevent loss of ammonia from Aug. 11 for the next 15 d. The monitoring was performed during Aug. 26 to Sep. 4, 2008 (9 d). It had been planned to monitor the summer stockpile for 15 d but monitoring had to be stopped on day 9 because the litter shed lay in the path of Hurricane Hannah and there was concern that the monitoring equipment could be damaged by the winds. In winter, the stockpile was built on Jan. 27, 2009 and ammonia emission monitoring began the same day for 15 d.

Comparison of ammonia emission from the summer vs. winter stockpiles allowed evaluation of temperature effects on ammonia generation and emission. However, it was recognized that other environmental factor such as wind speed and cake properties (e.g., TAN) would also effect emissions, and perhaps, mask the main (temperature) effect.

### **3.2.2 Cake sampling**

To characterize the initial cake properties, for the summer stockpile, three transects ( $x_1$ ,  $x_2$ , and  $x_3$ ) as shown in [Figure 3-3](#) were made. Three core samples (~0.17 m diameter) down to the concrete pad, were obtained from each transect ([Figure 3-3](#)) using a soil sampler. All three cake cores from one transect was mixed thoroughly using a shovel and a sample of ~150 g was obtained. The three cake samples from the summer stockpile were stored in labeled plastic bags and brought back on ice (to minimize microbial activity) to the Biological and Agricultural Engineering Environmental Analysis

Lab (EAL). In summer, the initial and final stockpile samples were obtained on Aug. 11 (the samples were obtained before covering the stockpile with tarp) and Sep. 5, 2008, respectively. The cake samples were analyzed for constituents listed in Table 3-1 . The beginning and ending cake characteristics were compared to see how stockpiling and ammonia emission during stockpiling affected cake properties.

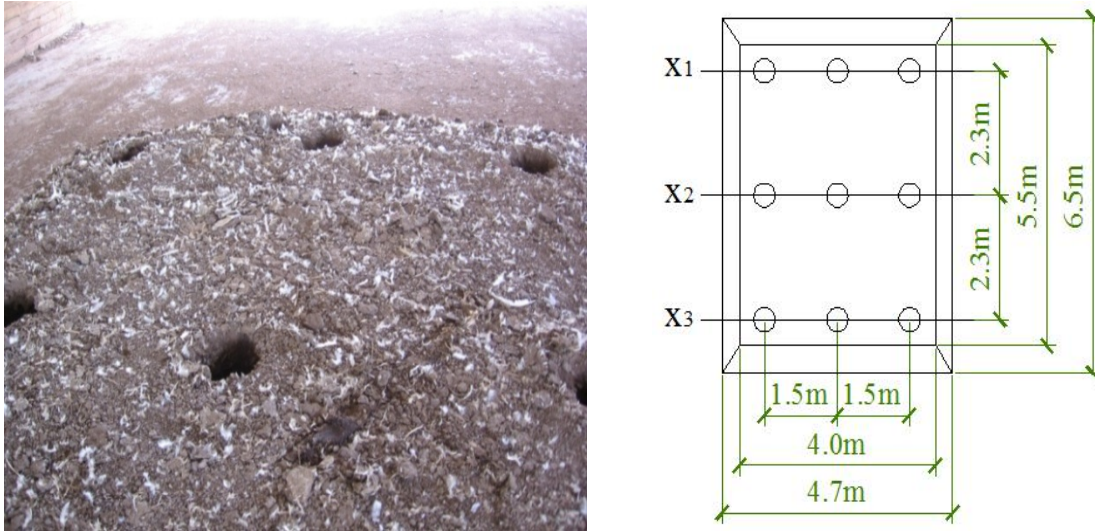


Figure 3-3 Cake sampling from stockpile (diameter of the core was 0.17 m)

In winter, the broiler cake stockpile was sampled more intensively than in the summer to quantify variations in N content with depth of the stockpile, as well as to obtain a better estimate of cake characteristics. The cake core sample representing the full depth of the stockpile (~1.1 m) was divided into three equal layers (~0.37 m each). Then the three cake samples from the same depth increment (layer) from the same transect (e.g.,  $x_1$ ) were composited to obtain a single sample. Thus, three depth increments were obtained for each transect, yielding nine samples in all for the stockpile both at the beginning (Jan. 27, 2009) and end (Feb. 11, 2009) of the winter study. In winter, sample preparation, handling, and analysis were the same as in summer.

**Table 3-1 Analytical methods used for analyses of broiler cake constituents**

Parameter	Method	Method detection limit (MDL) (mg/L)	Solids extraction	Reference
TKN (Total Kjeldahl N)	Persulfate digestion and ammonia salicylate method	0.037	Digestion in block digester with catalyst (of K <sub>2</sub> SO <sub>4</sub> , CuSO <sub>4</sub> ·5H <sub>2</sub> O, and pumice) and H <sub>2</sub> SO <sub>4</sub> .	EPA Manual 351.2 (1979) with slight modifications including dialysis or Standard Methods 4500-N <sub>org</sub> B (1998)
NH <sub>3</sub> -N (TAN)	Ammonia-salicylate method	0.016 for 0-2 mg/L; 0.124 for 0-100 mg/L	1.25 N K <sub>2</sub> SO <sub>4</sub> ; 10 g sample; 100 mL K <sub>2</sub> SO <sub>4</sub> ; shake 30 min; fast filter	EPA Method 351.2 (1979) or Standard Methods 4500-NH <sub>3</sub> G (1998), with slight modifications including dialysis
NO <sub>3</sub> <sup>-</sup> -N	Cadmium reduction method	0.011	1.25 N K <sub>2</sub> SO <sub>4</sub> ; 10 g sample; 100 mL K <sub>2</sub> SO <sub>4</sub> ; shake 30 min; fast filter	EPA Method 351.2 (1979), Technicon Industrial Method No. 100-70W (1973), or Standard Methods 4500-NO <sub>3</sub> <sup>-</sup> E (1998), with slight modifications including dialysis
pH	Electrometric method	Not available	Not available	EPA Method 150.1 (1979) or Standard Methods 4500-H <sup>+</sup> B pH Value (1998)
TS (Total solids)	Gravimetric method (oven drying at 70 °C)	Not available	Not available	EPA Methods 160.1-160.4 (1979) or Standard Methods 2540 (1998)

In the winter stockpiling, the three samples from each layer (i.e., one from each transect) were assumed to be replicates. While the locations of the core samples were not selected randomly the cake was mixed thoroughly prior to stockpiling. The analyses of TKN, TAN, NO<sub>3</sub><sup>-</sup>/NO<sub>2</sub><sup>-</sup>-N, and pH of each layer were compared using t-test ( $\alpha = 0.05$ ) at beginning and end of winter stockpiling to see if the concentrations changed during stockpiling.

### 3.2.3 Ammonia concentration measurement

The concentration of ammonia in the air above the stockpile was determined using acid scrubbers. In the winter study, the photoacoustic spectrophotometer was also used to measure real time ammonia concentration for the last 2 d. Both measurement methods are described below.

#### Scrubber

The acid scrubber consisted of a 75 mL glass culture tube containing 3% (w/v) boric acid solution (Figure 3-4). Air (2.5 L/min) was drawn into the acid scrubber with a vacuum pump (Make: Gast Manufacturing; Model: 10D1125-101-1052; Range: 0-4.3 L/min) and  $\text{NH}_3$  in the air was absorbed by the acid solution. A flow meter (Make: Gilmont Instruments; Model: GF-8321-1401; Range: 0-6.3 L/min; Accuracy:  $\pm 5\%$ ) was connected to the scrubber to monitor the airflow rate (Figure 3-4). The flow meter reading upstream ( $q_a$ ) of the scrubber gives the correct flow rate because the air is at atmospheric pressure (the flow meter is calibrated at atmospheric pressure) while the flow meter reading downstream ( $q_d$ ) of the scrubber overestimates air flow rate because of sub-atmospheric pressure. However, the flow meter was not placed upstream of the scrubber because ammonia and particulates could have damaged the flow meter. So, the calibration curve (eq. [3.1]) was developed under laboratory conditions to correct the air flow rate measured downstream (Shah et al., 2007). The relationship between the corrected average air flow rate and the average air flow rate read on the flow meter was developed from a test shown in Figure 3-4 in the lab. Different equations were used in summer vs. winter because a moisture trap was used in winter but not in summer.

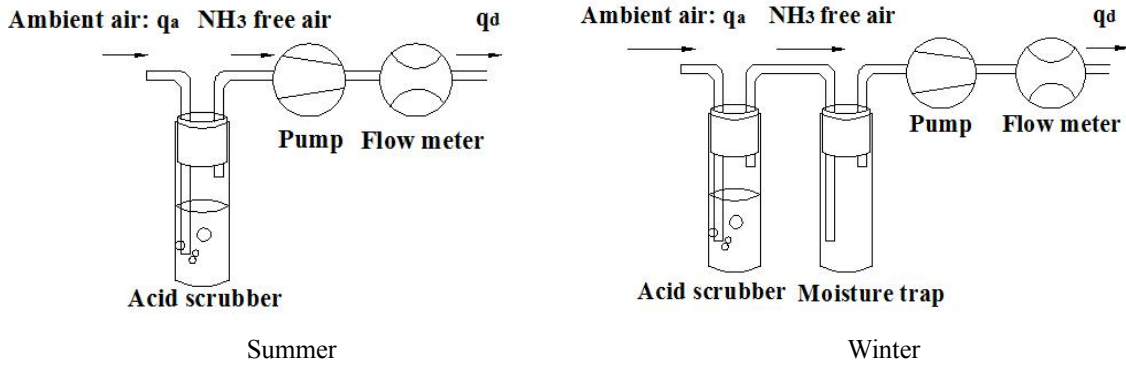


Figure 3-4 Acid scrubber arrangement used in summer and winter. The terms  $q_a$  and  $q_d$  represent airflow rates at atmospheric and sub atmospheric pressures.

$$q_a = 0.91q_d - 1.77 \quad \text{[summer]} \quad [3.1a]$$

$$q_a = 0.86q_d - 1.23 \quad \text{[winter]} \quad [3.2b]$$

where

$q_a$  = corrected average air flow rate through the scrubber at 21.1°C, m<sup>3</sup>/s; and

$q_d$  = average downwind air flow rate read on the flow meter at 21.1°C, m<sup>3</sup>/s.

The scrubber solution was replaced daily with fresh solution. The ‘spent’ scrubber solutions were analyzed for TAN (method and MDL were shown in Table 3-1). Air flow rate through the scrubber was measured at the beginning and end of the monitoring period by the flow meter and the average value was assigned to that scrubber for that monitoring period. As the flow meter is calibrated by the manufacturer at 21.1°C, the flow rate for the actual ambient temperature was corrected using the following equation.

$$q_{ac} = \frac{21.1 + 273.15}{T + 273.15} q_a \quad [3.3]$$

where

$q_{ac}$  = corrected average air flow rate, m<sup>3</sup>/s; and

T = average ambient air temperature during sampling period, °C.

Ammonia-N concentration in the air was calculated from the TAN concentration of the scrubber and air flow rate through the scrubber ( $q_a$ ) as shown in eq. [3.3].

$$C_{NH_3-N} = \frac{c_{NH_4^+-N} V_{acid}}{\Delta t q_{ac}} \quad [3.4]$$

where

$C_{NH_3-N}$  = average TAN concentration in air during sampling period, mg/m<sup>3</sup>;

$c_{NH_4^+-N}$  = TAN concentration in the acid scrubber solution, mg/m<sup>3</sup>;

$V_{acid}$  = volume of the acid solution in the scrubber, m<sup>3</sup>;

$\Delta t$  = duration of sampling, s; and

$q_{ac}$  = corrected average flow rate of air through the scrubber, m<sup>3</sup>/s.

During the summer and winter studies, the volume of the acid solution used in eq. [3.3] was based on the measured mass of solution brought back from the field, assuming that the specific gravity of the solution was 1. Since the scrubber solutions on 8/29, 9/1 - 9/4/2008 and 1/28 - 2/5/2009 were analyzed before they could be weighed, those missing mass data were replaced by available mass data on those days where air temperatures were similar. This approach was followed since the loss of scrubber solution volume was correlated with air temperature.

The PVC tubing (4.5 mm ID & 7.9 mm OD) used for each scrubber was 2.6 m long. Short lengths of tubing were used to minimize dead air and condensation and use of equal lengths of the tubing ensured the same pressure drop in all scrubbers. The flexible PVC tube was used instead of the more expensive Teflon® tubing because Teflon® does not minimize ammonia sorption compared with PVC (Shah *et al.*, 2006).

### **Photoacoustic spectrophotometer**

During the last 2 d of the winter study, a photoacoustic spectrophotometer (Table 3-2) was also deployed to monitor real time ammonia concentration at 0.15 m height above the surface of the stockpile (sampling interval of 2 min). The instrument was used to monitor diurnal variations in NH<sub>3</sub>

emissions. Since the instrument was brand-new and had been factory-calibrated, it was not calibrated in this study.

**Table 3-2 Specifications of photoacoustic field gas monitor**

Specifications	Details
Manufacturer	INNOVA
Model	1421
Accuracy	Not listed
Detection limit of ammonia	0.2 ppm at 20°C and 1 atmosphere of pressure
Dynamic range	4 orders of magnitude (i.e., 10000 times the detection limit at 5 selected sample integration times (S.I.T.))
Zero drift	±0.2 ppm per three month
Repeatability	1% of measured value
Range drift	± 2.5% of measured value per 3 months

### 3.2.4 Ammonia emission calculation

Gas emissions are usually controlled by mechanical transport as wind transports the gas away from the emitting surface (forced or mechanical convection). However, emissions can also occur in the absence of wind due to molecular diffusion (natural or free convection); natural convection can be affected by thermal gradient. Since ammonia emissions could have been due to these two mechanisms – forced and natural convection, a separate set of scrubbers was used for each mechanism (discussed later). While emissions due to forced convection is routinely measured using various methods, no literature on emission due to natural convection from liquid or solid waste stockpiles or surfaces could be located. The theory for measuring emissions from these two mechanisms is separately discussed below.

#### Theory of convective transport

To identify convective conditions (natural vs. forced), it is necessary to have an understanding of various dimensionless numbers, e.g. Grashof’s number, Reynolds number, and Richardson’s number. Grashof’s number (Gr) is used in heat transfer and to solve natural convection problems. It is expressed as (Karwe *et al.*, 2003):

$$Gr = \frac{g\beta\Delta TL_{Gr}^3\rho^2}{\mu^2} = \frac{g\beta\Delta TL_{Gr}^3}{\nu^2} \quad [3.5]$$

where

$g$ = acceleration due to gravity, 9.8 m/s<sup>2</sup>;

$\beta$ = volumetric thermal expansion coefficient;

$\Delta T$ = temperature difference, K;

$L_{Gr}$ = characteristic length, m;

$\rho$ =density of air, kg/m<sup>3</sup>;

$\mu$ =dynamic viscosity of air, Pa\*s; and

$\nu$ = $\mu/\rho$ , kinematic viscosity of air, m<sup>2</sup>/s.

The characteristic length ( $L_{GR}$ ) is the fetch in this study (described later). The expansion coefficient  $\beta$  at standard pressure ( $P$ ) is expressed shown in eq. [3.5]. However, it can be simplified for ideal gases as show in eq. [3.6] (ASHRAE, 2005):

$$\beta = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_p = \frac{1}{V} \frac{\Delta V}{\Delta T} \quad [3.6]$$

$$\beta = \frac{1}{T} \quad [3.7]$$

Reynold's number ( $Re$ ) is the ratio of the inertial force to viscous force of the fluid. It can be expressed as (Kays *et al.*, 2005):

$$Re = \frac{uL_{Re}}{\nu} \quad [3.8]$$

where

$u$ = wind speed, m/s;

$L_{Re}$ = characteristic length, m; and

$\nu$ = kinematic viscosity of air, m<sup>2</sup>/s.

The characteristic length ( $L_{RE}$ ) in this study is the fetch (discussed later). In thermal convection, the Richardson's number ( $Ri$ ) is a measure of the relative importance of natural convection to forced convection. It can be expressed in terms of  $Gr$  and  $Re$  (Kays *et al.*, 2005) as shown below.

$$Ri = \frac{Gr}{Re^2} \quad [3.9]$$

The criteria to separate the forced and natural convections based on the Richardson's number are expressed as (Kays *et al.*, 2005):

- (a)  $Ri < 0.3$ : natural convection is negligible;
- (b)  $Ri > 16$ : forced convection is negligible; and
- (c)  $0.3 < Ri < 16$ : both types of convection (referred here as mixed convection) may be present.

However, running both sets of scrubbers when  $0.3 < Ri < 16$  would have caused confounding. So the above criteria were modified as:

- (i)  $Ri < 0.3$ : Forced convection scrubbers;
- (ii)  $Ri > 16$ : natural convection scrubbers; and
- (iii)  $0.3 < Ri < 16$ : mixed convection; if transitioning from natural to mixed convection, natural convection was assumed. If transitioning from forced to mixed convection, forced convection was assumed.

### **Identification of convective conditions in the field**

Five ultrasonic anemometers (four 2-D and one 3-D) were used to record wind speeds at five heights (0.15, 0.45, 0.75, 1.25, and 1.95 m) above the stockpile. In summer, wind speed was measured every 1.5 s and the average for 3 s was stored in the data logger (Make: Campbell Scientific, Logan, UT; Model: CR1000) whereas in winter, wind speed was measured every 2 s and stored in data logger. The 3-D anemometer was located at 0.75-m height and it measured horizontal wind speed and direction, and vertical wind speed. The 2-D anemometers were only used to monitor the horizontal wind speed. The anemometers' specifications are shown in Table 3-3. All of the anemometers were located at the center of the stockpile on a mast.

**Table 3-3 Ultrasonic anemometers' specifications**

Manufacturer	Type & model	No.	Location above stockpile	Range	Accuracy	Output Resolution	Output Signal
Gill Instruments	2-D (Windsonic1-L)	2	0.15 m & 0.45 m	0-60 m/s (WS <sup>a</sup> )	±2% of reading (WS)	0.01 m/s (WS)	RS-232
R. M. Young Company	2-D (85000)	2	1.25 m & 1.95 m	0-70 m/s (WS)	WS: ±2% for 0-30 m/s ±3% for 30-70 m/s	0.1 m/s (WS)	SDI-12
R. M. Young Company	3-D (81000)	1	0.75 m	0-40 m/s (WS) WD <sup>b</sup> : 0.0-359.9° (azimuth), ±60.0° (elevation)	WS: ±1% rms ±0.05 m/s for 0-30 m/s ±3% rms for 30-70 m/s WD: ±2° for 1-30 m/s ±5° for 30-70 m/s	WS: 0.01 m/s WD: 0.1°	RS-232

<sup>a</sup> WS: Windspeed

<sup>b</sup> WD: Wind direction

In the field, to separate emissions due to forced (mechanical) vs. free (natural convection) the following conditions were identified as listed below. The flow of logic for controlling the scrubbers for different convective conditions is shown in Figure 3-5, The program for the data logger is presented in Appendix A.

- (a) Deposition: When the vertical wind speed was downward and horizontal wind speed was zero, it was assumed that there was ammonia deposition and dummy scrubbers (discussed later) were activated.
- (b) Forced (mechanical) convection: Forced convection scrubbers (discussed later) were activated when (1) vertical wind direction was downward and horizontal wind speed was  $>0$  m/s and (2) when the vertical wind direction was upward and  $Ri < 0.3$ .
- (c) Free (natural) convection: Free convection scrubbers (discussed later) were activated when (1) both the vertical and horizontal wind speeds were zero, and (2) the vertical wind direction was upward and  $Ri > 16$ .

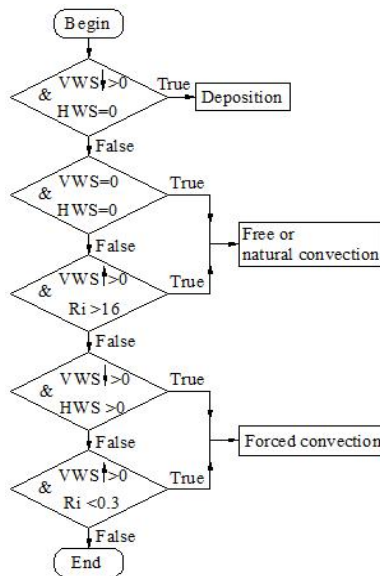


Figure 3-5 Flow of logic used to control operation of the scrubbers (VWS: vertical wind speed, ↑: vertical wind direction was upward, ↓: vertical wind direction was downward, HWS: horizontal wind speed, Ri: Richardson’s number)

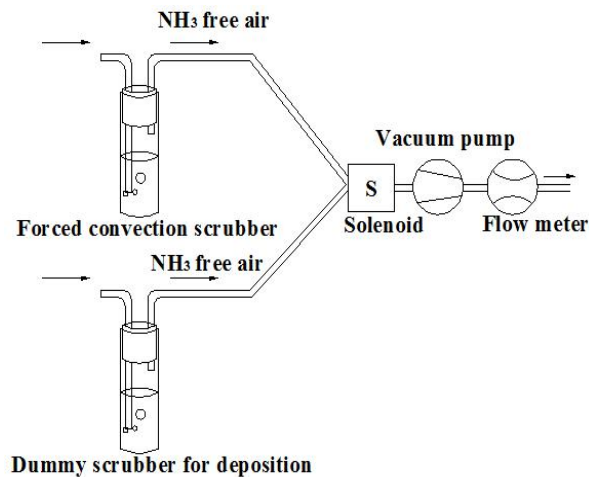
From the flow chart (Figure 3-5), it is clear that when vertical wind speed was downward and  $0.3 < Ri < 16$ , the logic cycle stopped and the port status remained unchanged. Even when the previous condition was deposition, it remained unchanged which happened  $< 5\%$  during the field study.

The flow of logic was controlled by two ports (7 & 8) on the CR 1000 data logger. This data logger also recorded wind and temperature (discussed later). The status of the ports on the data logger is shown in Table 3-4.

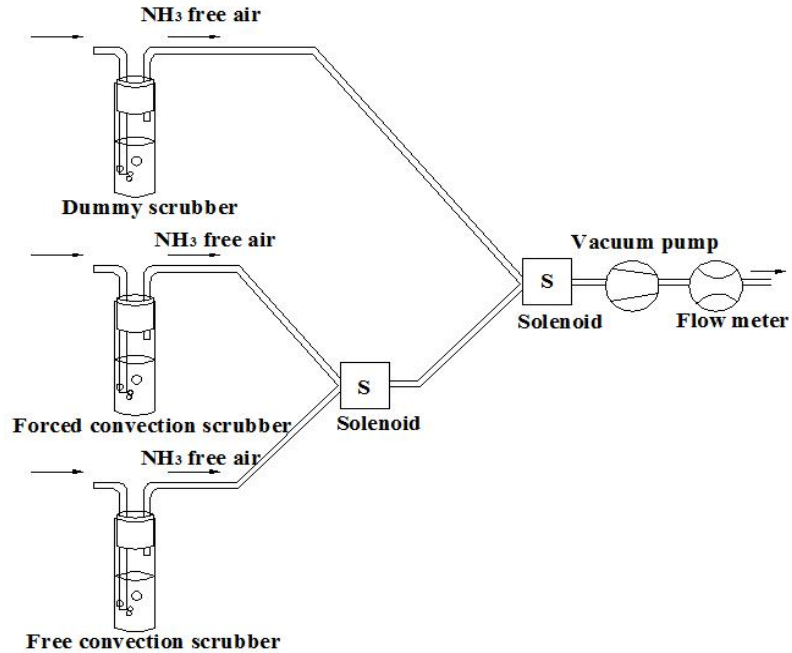
**Table 3-4 Status of ports in the CR 1000 data logger used to control scrubber operations**

Port	Status	
	7	8
Deposition	0	0
Free (natural)	1	1
Forced	1	0

In the field, there were scrubbers for deposition and forced convection at all five heights. Only the lowest two heights had scrubbers for free convection. Solenoids were used to change the air flow direction to different scrubbers (Figure 3-6). The schematic of the scrubber system for upper three heights (0.75, 1.25, and 1.95 m) is shown in Figure 3-6 while the schematic of the scrubber system for the lower two heights (0.15 and 0.45 m) is shown in Figure 3-7.



**Figure 3-6 Combination of forced convection and dummy scrubbers (upper three heights)**



**Figure 3-7 Combination of forced convection, free convection, and dummy scrubbers (lower two heights)**

It was assumed that the pressure above the stockpile was 1 atm. The wind speed, wind direction and temperature (discussed later) at 0.75 m height were used to calculate  $Re$ ,  $Gr$  and  $Ri$ . The characteristic length (fetch) used for  $Gr$  and  $Re$  calculations was determined based on wind direction monitored by the 3-D anemometer and the dimension of the stockpile. The fetch was calculated based on the foot print dimension of the stockpile.

Two thermistors (Make: OMEGA; Model: 44212; Accuracy:  $\pm 0.1$  °C; Range: -50 °C to 50 °C; Time constant: 10 s in free still air) at 0.55 and 0.95 m above the surface of the stockpile were used to measure temperatures required for  $Gr$  calculation (eq. [3.4] & [3.6]). In a preliminary test over the stockpile using four thermistors, it was observed that the temperature changed linearly with height. So, temperature at 0.75 m was assumed to be the average of the temperatures measured at 0.55 m and 0.95 m. Even though a thermistor has a longer response time than a thermocouple, it is more accurate. Since the temperature difference between 0.55 and 0.95 m heights was very small, the thermistor was considered to a better choice than the thermocouple.

All data monitored by the anemometers and thermistors was recorded on the CR1000 data logger. In summer, the data logger recorded the data every 3 s (based on two 1.5-s data points). In winter, the data logger recorded data every 2 s (measurement interval of 2 s). After Gr, Re, and Ri were calculated by the data logger, it identified forced, natural and deposition conditions and operated the solenoids accordingly (Figure 3-5, Table 3-4). Thus, for each condition, a specific set of scrubbers was operated.

**Calculation of ammonia emission under natural convection:**

When there is no wind, emission will be due to molecular diffusion and will be controlled by the gas concentration gradient. This diffusive transport will be further expedited by natural convection as the warm air rises. For natural convection, Fick’s first law can be used to calculate emission as (eq. [3.9]):

$$J_n = -D \frac{\Delta C}{\Delta z} \tag{3.10}$$

where

$J_n$ = NH<sub>3</sub> emission due to natural convection, mg/m<sup>2</sup>-s;

$D$ = molecular diffusion coefficient or diffusivity of ammonia, m<sup>2</sup>/s;

$\Delta C$ = the difference in NH<sub>3</sub> concentration at two heights (0.15 m & 0.45 m), mg/m<sup>3</sup>; and

$\Delta z$ = the distance between the two heights (0.3 m), m.

Molecular diffusivity increases with temperature following Stokes-Einstein equation (Welty, 1984)

as shown below.

$$\frac{D_{T1}}{D_{T2}} = \left( \frac{T_1}{T_2} \right)^{1.5} \tag{3.11}$$

where

$T$ = temperature, K.

At 298 K, ammonia diffusivity in air is  $2.8 \times 10^{-5} \text{ m}^2/\text{s}$  (Incropera and DeWitt, 1990). The ammonia diffusivity at any other temperature can be calculated using eq. [3.10]. Based on calculated temperature at 0.75 m, ammonia diffusivity at that height was calculated based on the modified equation [3.11].

$$D_{0.75} = \left( \frac{T_{0.75}}{298} \right)^{1.5} D_{298} \quad [3.12]$$

where

$T_{0.75\text{m}}$  = temperature at 0.75 m, K; and

$D_{298\text{K}}$  = ammonia diffusivity at 298 K in air,  $\text{m}^2/\text{s}$ .

### Calculation of ammonia emission under forced convection

The integrated horizontal flux (IHF) method, a micrometeorological method, was used to measure emission due to forced convection. This method is not intrusive, and has high reliability (Shah *et al.*, 2006). Ammonia flux using the IHF method (Denmead, 1983) is calculated as:

$$J_m = \frac{1}{x} \int_{z_0}^{z_p} \bar{C} \bar{u} dz \quad [3.13]$$

where

$J_m$  = ammonia flux due to forced (mechanical) convection,  $\text{mg}/\text{m}^2\text{-s}$ ;

$x$  = fetch, m;

$z_0$  = roughness length, m;

$z_p$  = height of the profile development, m;

$\bar{u}$  = average horizontal wind speed at the height  $z$  over the sampling period, m/s; and

$\bar{C}$  = average gas concentration at height  $z$  over the sampling period,  $\text{mg}/\text{m}^3$ .

In this study eq. [3.12] was modified to:

$$J_m = \frac{1}{x} \sum_{i=1}^n \bar{C}_i \bar{u}_i \Delta z_i \quad [3.14]$$

where

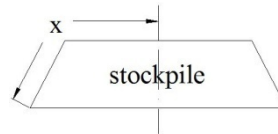
$n$  = the number of height at which gas concentrations and wind speeds are monitored;

$\bar{C}_i$  = average concentration of  $\text{NH}_3$  at  $i^{\text{th}}$  height during the sampling duration,  $\text{mg}/\text{m}^3$ ;

$\bar{u}_i$  = average wind speed at height  $z_i$ ,  $\text{m}/\text{s}$ ; and

$\Delta z$  = the height increment.

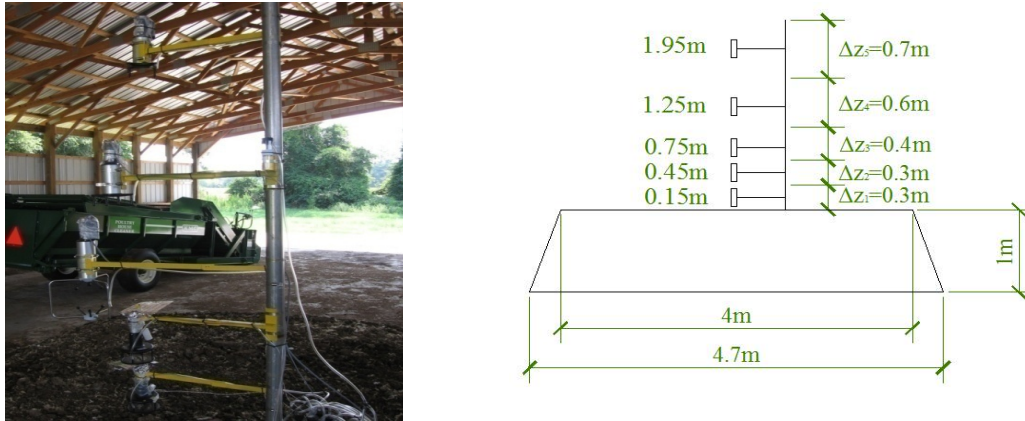
The fetch ( $x$ ) used in eq. [3.13] was assumed to be the distance that wind traveled over the surface of the stockpile and not just the horizontal projection from the edge of the stockpile to the center (Figure 3-8). While the wind velocity profile should not change once it enters the fetch (i.e., the leading edge of the stockpile), that is unavoidable in a trapezoidal stockpile. Assuming the horizontal projection as fetch would have resulted in overestimation of emission, the approach proposed here may result in slight underestimation of emission.



**Figure 3-8 Fetch over the stockpile**

Sutton (1953) reported that  $z_p$  was equal to the square root of fetch ( $x$ ). In this research, the foot print of the stockpile was 4.7 m by 6.5 m. So, based on the range of  $x$  that varied between 2.35 m (half of stockpile width) and 4 m (half of the diagonal of the stockpile), a  $z_p$  value of 1.5 to 2 m was considered acceptable. Gas concentrations (using scrubbers) and wind speed (using ultrasonic anemometers) were measured at five heights (Figure 3-9) - 0.15 m, 0.45 m, 0.75 m, 1.25 m, and 1.95 m from the surface of the stockpile. A minimum of five heights for monitoring  $\bar{C}_i$  and  $\bar{u}_i$  was recommended by Sommer *et al.* (2004). These measurement heights gave  $\Delta z_1$ ,  $\Delta z_2$ ,  $\Delta z_3$ ,  $\Delta z_4$ , and  $\Delta z_5$  values of 0.3 m, 0.3 m, 0.4 m, 0.6 m, and 0.7 m, respectively. Hence the  $z_p$  in this study was 2.3 m. As the concentration would be higher closer the stockpile surface than in the air above, measurements were taken more intensively closer to the surface. As discussed earlier, these scrubbers drew air only when the criterion for forced convection was satisfied. There was a blank scrubber which was placed

with the scrubbers at the base of the mast. This blank was used as baseline to adjust the ammonia concentrations in the forced and natural scrubbers for contamination during preparation and transportation.



**Figure 3-9 Location of the scrubbers and anemometers above the broiler cake stockpile**

During the winter study, after 3 d all scrubbers were placed inside a cooler to prevent freezing. The cooler was equipped with two 4-W light bulbs that turned on when the temperature dropped below 4 °C to prevent freezing of the scrubbers.

During the field study, the background concentrations were not monitored as is usually done in micrometeorological studies over land-application sites. The broilers were ~2 weeks of age at the start of the summer study and the closest ventilation fan (Figure 3-1) which was in operation for part of the time, was exhausting air parallel to the shed but ~12-13 m to the side of the shed. However, the predominant wind direction during the summer was from the ESE which would have pushed the exhaust air away from the shed, thus reducing contamination of the air inside the shed with ammonia from the broiler house. During the winter study, broiler chicks were placed 1 d before the study ended. With the small chicks and cold weather, the minimum ventilation fan closest to the shed was running on the timer. Hence, even in winter chances of contamination of the shed air by ammonia from the broiler house was low.

In summer, the ammonia concentration at the lower two heights for forced convection were discarded for the first 2 d (Aug. 27 & 28, 2008) because of the failure of the solenoids. In winter, the data for Feb. 1, 2009 was lost because the acid solution inside the scrubber froze. The data for Feb. 7, 2009 was also discarded as it ran for only 3.5 h during the warmer part of the day (13:22-15:05) because the power was mistakenly disconnected by a farm worker. Missing ammonia concentration data for a particular height was estimated by fitting a trend line (2<sup>nd</sup> order polynomial) through the available ammonia concentration data for the other heights for that day. Comparison of the values based on measured and estimated data are discussed in Chapter 4 (Results and Discussion).

### Calculation of emission and emission factors

The flux due to natural and forced convections were added to obtain total ammonia-N emitted per unit area per unit time (flux) ( $\frac{kg}{m^2-d}$ ). Ammonia-N emission were also calculated per unit mass of cake per unit time ( $\frac{kg}{Mg-d}$ ), per unit volume of cake per unit time ( $\frac{kg}{m^3-d}$ ), per animal unit (AU= 500 kg) per unit time ( $\frac{kg}{AU-d}$ ), as well as percent of total N in the broiler cake stockpile.

## 3.3 Chamber study

### 3.3.1 Treatments

Broiler cake was brought to the laboratory on Oct. 20, 2008 from the broiler farm and stored in two sealed plastic containers in the freezer. On Oct. 28, 2008, the cake was mixed thoroughly using a shovel and passed through a sieve (0.02 m × 0.02 m holes) to remove large clumps and feathers. Thereafter, the cake was again stored in the freezer until start of the experiment. On Nov. 4, the cake was removed from the freezer to bring it up to room temperature prior to the study. The first trial (started on Nov. 5) failed and its results had to be discarded (discussed later). Between the first trial

and the beginning of the actual study, the cake was left in the plastic container with lid at ambient temperature under a shed. The actual study began on Nov. 11 and ended on Nov. 24, 2008.

There were three treatments in this study: control, cover and double depth (uncovered). Each treatment had three replicates. The control and cover (Treatment 1) treatments used 700 g of cake per replicate, and the double depth (Treatment 2) treatment had 1400 g of cake. Prior to placement in the chamber, for control and treatment1, ~900 g cake was transferred from the plastic container into a bucket and mixed. Thereafter, 700 g of the cake was weighed and packed into a PVC container (0.07 m depth and 0.16 m diameter) while a sample of the cake (160 g) was placed in a plastic bag for lab analysis. For Treatment 2, ~1400 g of cake was packed into the PVC container and ~160 g set aside for lab analysis following the procedure used for control and treatment 1.

### **3.3.2 Chamber description**

Nine plastic buckets (capacity: 13.2 L or 3.5 gal.; 0.25 m height; 0.26 m diameter at the base and 0.3 m diameter at the top) with tight-fitting lids were used as chambers in this experiment (Figure 3-10). Each chamber had PVC tubing (4.8 mm ID and 7.9 mm OD) on the top of the lid as outlet (Figure 3-11). The PVC tubing was connected to a polycarbonate volumetric flask (acid scrubber) which contained 250 mL 3%w/v boric acid solution (Figure 3-11). There were four 6.25 mm holes, diagonally placed at ~0.165 m height in each chamber to bring in ambient air. The holes were covered with 6.5 mm thick carbon filter (double layer) to prevent ambient ammonia from entering or the ammonia inside from leaving the chamber.

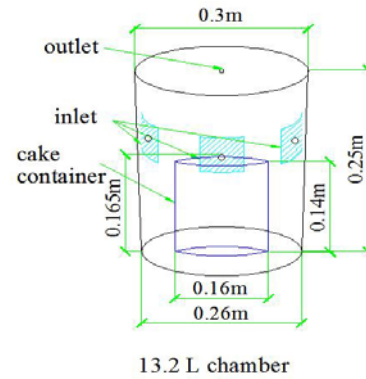


Figure 3-10 Cake container inside the chamber

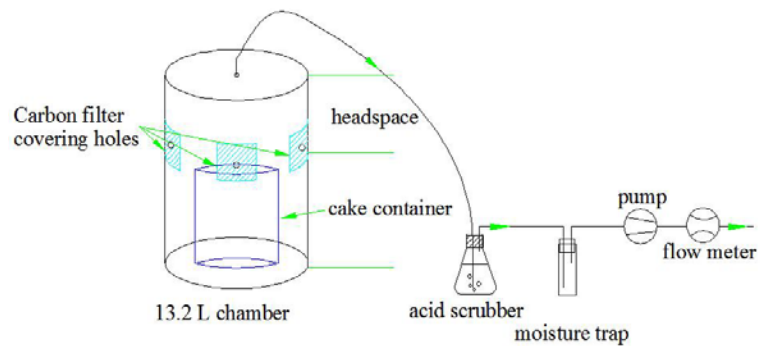
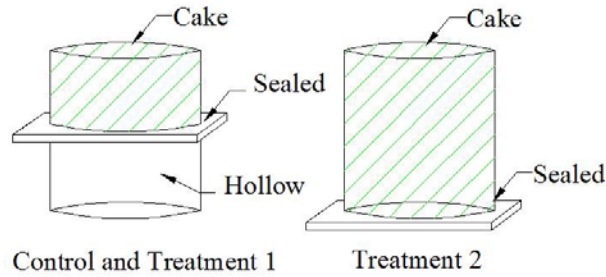


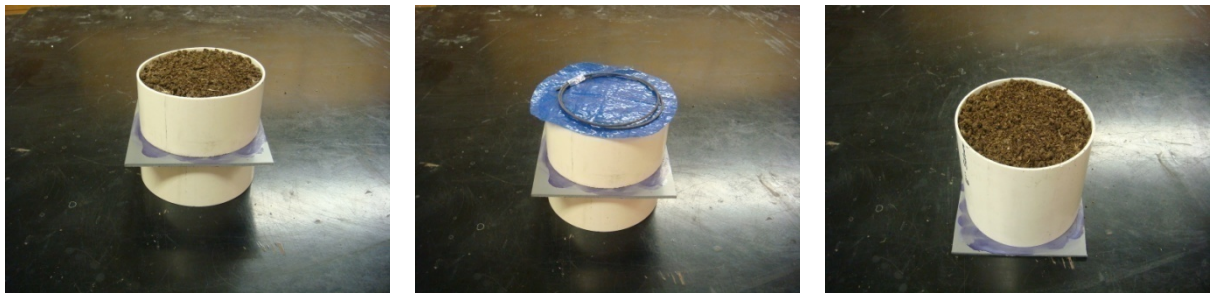
Figure 3-11 Schematic of air sampling system used in the chamber study

The PVC container, containing the broiler cake was placed in the middle of the chamber as shown in Figure 3-10. The PVC containers in the control and cover (Treatment 1) treatments were placed on ~0.16-m PVC pipe sections (Figure 3-13). This ensured that the surface of the broiler cake in all the treatments were at the same height from the chamber bottom; thus the height of air inlet with respect to the cake surface was not a confounding factor. The connection of the PVC tube and the board were sealed as shown in Figure 3-12.



**Figure 3-12 Construction of PVC tube used in the chamber study**

In Treatment 1 (cover), a circular piece of tarpaulin (~0.2 m diameter) was used to cover the cake surface. The tarp cover was held in place with a metal ring of the same diameter. After all of the treatments were prepared, the chambers were sealed.



Control

Treatment 1 (Cover)

Treatment 2 (Double depth)

**Figure 3-13 Broiler cake treatments in the chamber study**

In an earlier trial, 2.5 kg of broiler cake had been placed at the bottom of the buckets in control and Treatment 1 and 4.0 kg in Treatment 2. However, because of the relatively large quantities of cake used, there was excessive ammonia production, resulting in rapid breakthrough of ammonia through the acid scrubbers. Therefore, to continue using the buckets (chambers), cake was packed in PVC containers in this study to reduce the total mass of the cake.

### 3.3.3 Chamber operation

Ammonia-laden air was drawn through the acid scrubber using a vacuum pump with an air flow rate 1.8 L/min. Ammonia emitted from the chamber was collected in the scrubber. A flow meter was connected downstream of the scrubber to monitor the airflow rate (Figure 3-11). As discussed earlier, a

calibration curve developed in the lab was used to correct the air flow rate measured downstream. The scrubbers were replaced daily (~24 h) with fresh solution. The 'spent' scrubber solutions were analyzed for TAN (method and MDL are shown in [Table 3-1](#)), as in the field study.

The vacuum pumps were run at 25% duty cycle (15 min on and 45 min off) using a timer for 14 d. The timer was used to prevent overloading of the acid scrubbers. In the earlier (abandoned) trial, apart from the larger mass of cake used, airflow rate was higher (2 L/min) and the pumps were operated on 75% duty cycle (45 min on and 15 min off). Consequently, in the abandoned trial, the smell of ammonia in the lb was strong; however, in the second trial (Nov. 11 to Nov. 24, 2008), there was no ammonia smell in the lab. Further, sporadic testing around the chambers using gas tubes (MDL = 1 ppm), detected no measurable levels. With the intermittent vacuum pump operation, there was some concern that ammonia might have diffused out of the chamber through the inlet holes (covered with C filter) due to molecular diffusion when the pump was not running. Since molecular diffusion is a much slower process than turbulent diffusion (due to air movement), any leakage would have been small enough to be not detected by the gas tubes. As shown in [Figure 3-12](#), the hollow spaces beneath the control and Treatment 1 could have accumulated ammonia when the pump was not running. It is unlikely that the accumulation of ammonia in those hollow spaces in these two treatments would have affected the results because much of the accumulated ammonia would have been flushed out when the pump was running. Further, since this study ran for 14 d and ammonia concentrations in the scrubbers were time-averaged, any error due to accumulation in the hollow space would likely have been too small to affect the results.

Because the cake or litter stockpiles would likely be inside sheds or covered, they would likely experience lower wind speeds than if they were placed outside, uncovered. So, with the pump running, a longer residence time of 5.8 min (flow rate: 1.8 L/min) was used compared with 2.2 min in [Tasistro](#)

*et al.* (2007) and 5.1 min in *Liu et al.* (2007) and *Wang et al.* (2006). With the vacuum pump running, the air exchange rate was 0.17 volumes/min.

During the first 3 d, a 50 mL 3% boric acid scrubber was used in place of the moisture trap (Figure 3-11) to minimize ammonia escape and quantify the efficiency of the scrubber. Hence, it was assumed that no ammonia escaped through the secondary scrubber. The primary scrubber's efficiency ( $\eta$ ) was calculated as:

$$\eta = \frac{m_1}{m_{total}} \quad [3.15]$$

where

$m_1$ =ammonia mass trapped in the primary scrubber, mg.

$m_{total}$ = ammonia mass trapped in both scrubbers, mg.

A linear regression of scrubber efficiency vs. ammonia concentration was developed for the primary scrubber. While the efficiency evaluation was only performed for the 3 d, there were a total of 27 data points representing a wide range of concentrations (discussed in Chapter 4). Because scrubber efficiency was very high, ammonia concentrations were not adjusted for scrubber efficiency while comparing the treatments.

The ammonia flux from the chamber was calculated as:

$$J_c = \frac{qC_{NH_3}}{A} \quad [3.16]$$

where

$J_c$  = ammonia flux from chamber, mg/m<sup>2</sup>-s;

$q$ = air flow rate, m<sup>3</sup>/s;

$C_{NH_3}$  = average outlet NH<sub>3</sub> concentration, mg/m<sup>3</sup>; and

$A$ = area of the cake surface, m<sup>2</sup>.

Average outlet NH<sub>3</sub> concentration was calculated using eq. [3.3], also used for the field study. At the end of the experiment, the cake from each replicates was mixed thoroughly in a separate bucket and sampled for analysis. In total, nine samples were collected in labeled plastic bags and taken to the Environmental Analysis Lab (EAL) at the Department of Biological and Agricultural Engineering for analysis of the same constituents as in the field study (Table 3-1).

### 3.3.4 Statistical analyses

Statistical analysis linear mixed models were considered for ammonia concentrations/fluxes with fixed effects for treatment, time and their interaction, and random effects for the PVC containers, nested within treatment. An autoregressive correlation structure was assumed so that the correlation between two observations from the same replicate, measured x days apart were modeled as have correlation  $\rho^d$ , while observations on different replicates were assumed to be independent. Models were fit using the mixed procedure with the SAS statistical software package (SAS, 2008). The change in ammonia flux over time for the three treatments was compared using repeated measures ANOVA; if the null hypothesis was rejected (i.e., if at least one treatment was different), the Tukey's test was used for least square means comparison (SAS, 2008). The GLM method was used to test the ammonia emission difference based on the three treatments for the first 7 d as well as for the entire study (13 d). An alpha value of 0.05 was used throughout the study.

## 4 RESULTS AND DISCUSSION

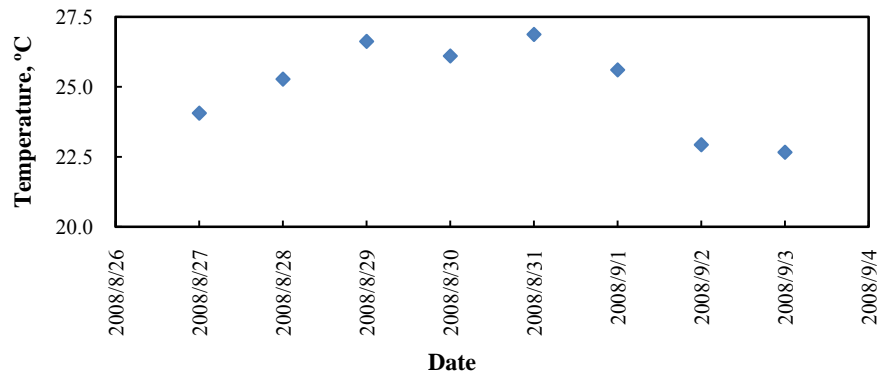
The results of the field study and chamber study are presented and discussed in this chapter. In the field study, ammonia emission factors were measured in summer and winter. In the chamber study, relative ammonia emissions from three treatments were compared.

### 4.1 Field study

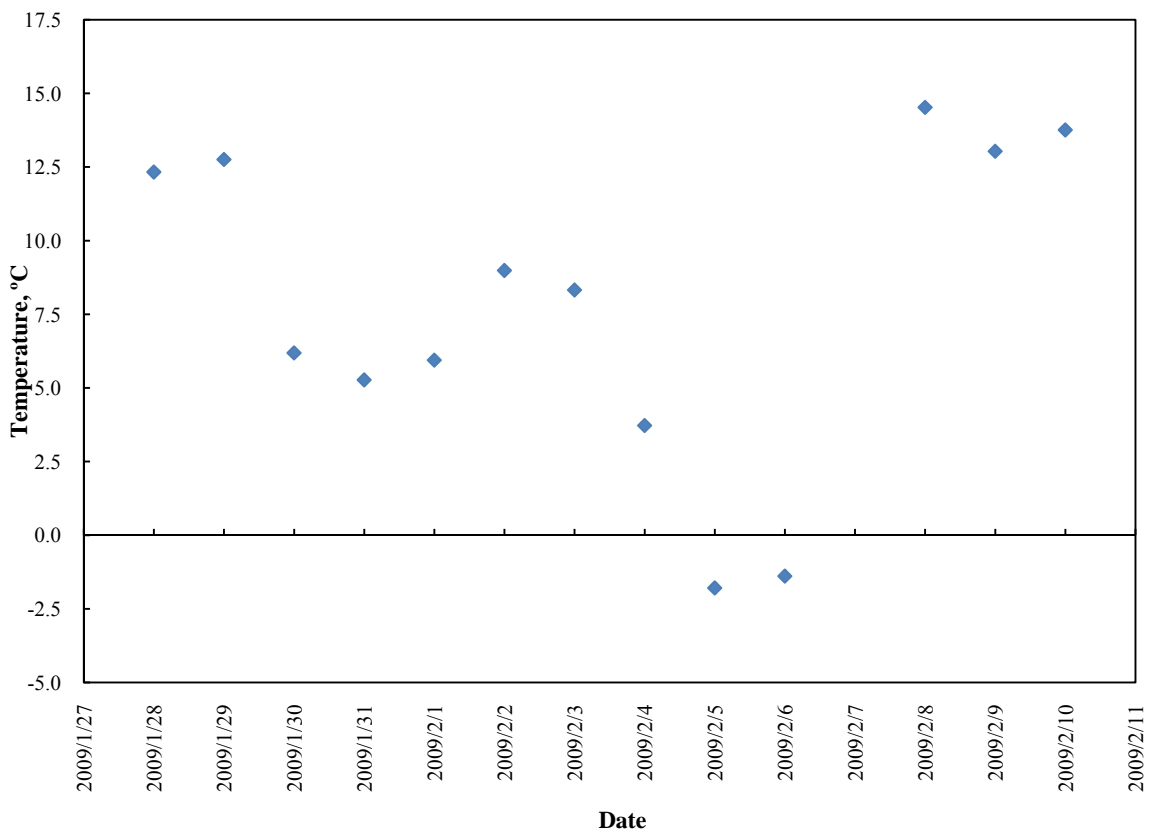
The summer (Aug. 27-Sep. 4, 2008) study had to be shortened to 9 d because of hurricane Hanna. In winter (Jan. 27-Feb. 11, 2009), the study lasted for 15 d. During the winter study, the data for 2/1/2009 was lost because the acid solution inside the scrubbers froze. Except for a 3.5 h period (13:22-17:05), data for 2/7/2009 was lost because the power was mistakenly disconnected by a farm worker. There were also other days when data for one or two scrubbers were lost and those discussed later. The missing data were estimated based on the data for the preceding and following days. When concentration for a particular scrubber was lost, it was estimated through extrapolation from measured concentration data at other heights. The measured and estimated data is compared later.

#### 4.1.1 Air temperatures over the stockpiles

The temperature was measured 0.55 m and 0.95 m above the stockpile surface using thermistors. The temperatures presented in [Figure 4-1](#) were the average of these two temperatures. In the summer study, the average daily temperature was 24.9 °C and ranged from 22.7 °C to 26.9 °C. In winter, the average daily temperature was 8.7 °C and ranged from -1.4 °C to 17 °C. The variability in temperature in winter was much higher than in summer. For reference, the 10-yr average daily temperatures in Tar Heel, NC, during the summer and winter study periods were 25.3 °C and 7.7 °C, respectively ([Weather Underground](#)).



(a) Summer



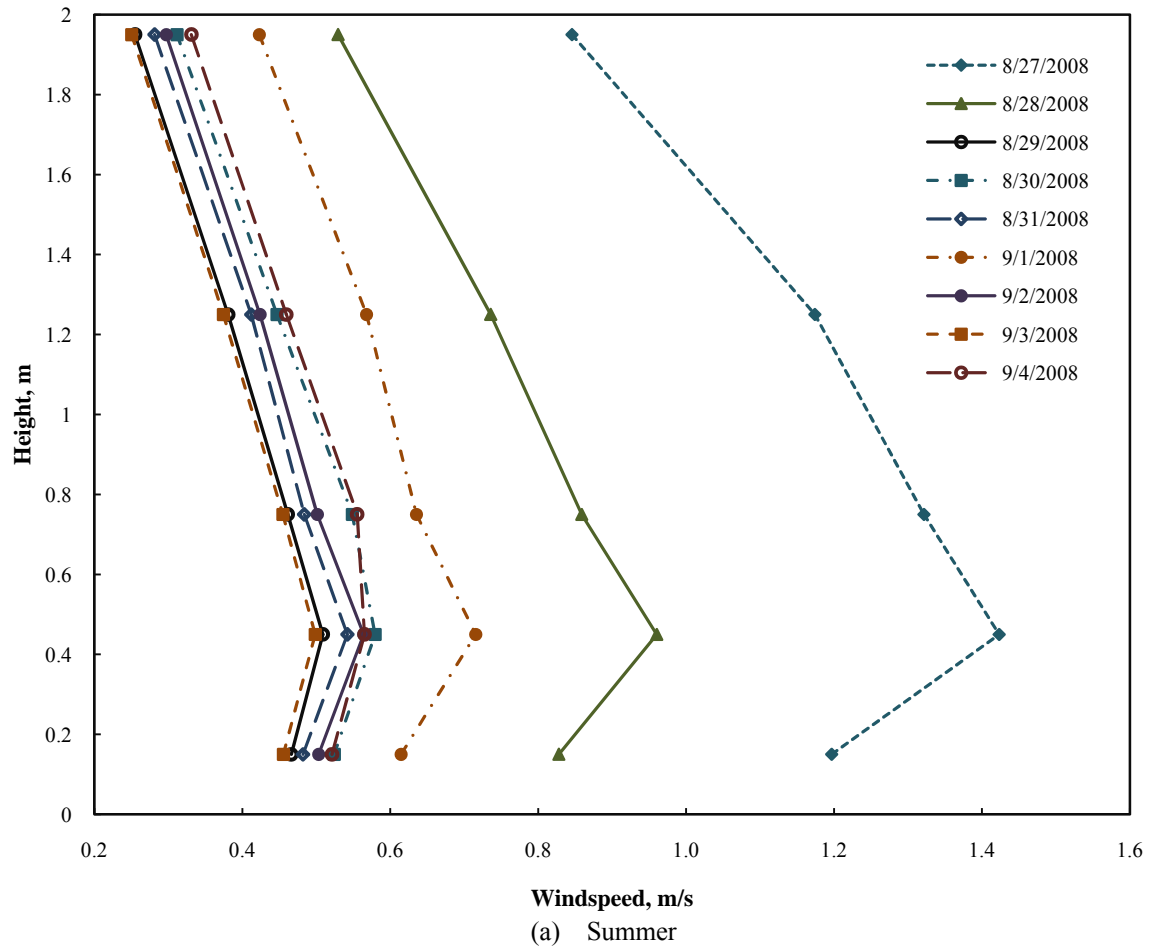
(b) Winter

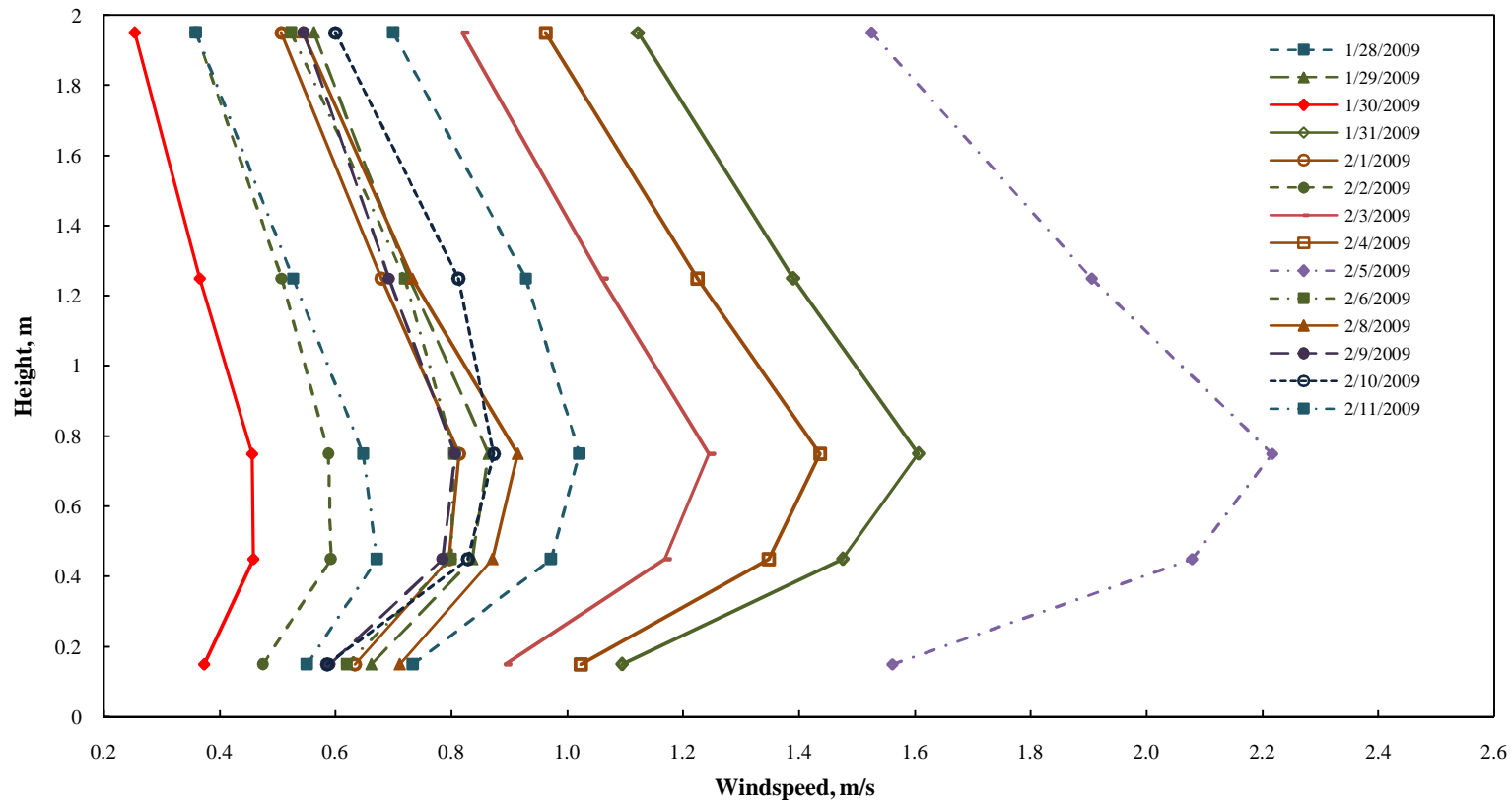
**Figure 4-1 Average daily temperature over the broiler cake stockpile surface during the (a) Summer and (b) Winter studies obtained by averaging temperature measured at 0.55 and 0.95 m above the broiler cake stockpile. Each data point is the average of temperature measurement made every 1.5 s in summer and 2 s in winter for the entire day. The temperature for 2/7/2009 was discarded because of the short period of record (3.5 h).**

#### **4.1.2 Wind speed and direction**

Horizontal wind speeds were measured at five heights (0.15, 0.45, 0.75, 1.25 and 1.95 m) above the stockpile as described in Chapter 3. Average daily wind speed profiles over the broiler cake stockpile are shown in [Figure 4-2](#).

Figure 4-2 Horizontal wind speed profiles over the broiler cake stockpile surface during (a) Summer and (b) Winter. Each data point in summer is the average of ~28,800 3-s readings while in winter it is the average of ~43,200 2-s readings. Data for 2/7/2009 was discarded because of short period of record (3.5 h). The wind speeds at adjacent heights are connected by line to indicate trend.





(b) Winter

Figure 4-2 indicates that the wind speed during the winter study period was higher than in summer. The daily wind profiles above the stockpile in summer and winter were somewhat similar except that in winter the wind speed was maximum at 0.75 m height, while in summer it was maximum at 0.45 m. This increase in wind speed up to a certain height above the stockpile was due to the compression of flow lines as the wind traveled over the sides of the stockpile before reaching the flat surface. Over an open flat surface, horizontal wind speed increases logarithmically with height for several meters above a zero plane (Loomis and Connor, 1992). But in this study, decline in wind speed at a height of 0.45 m above the stockpile surface in summer and 0.75 m in winter was due to the effect of the roof of the shed.

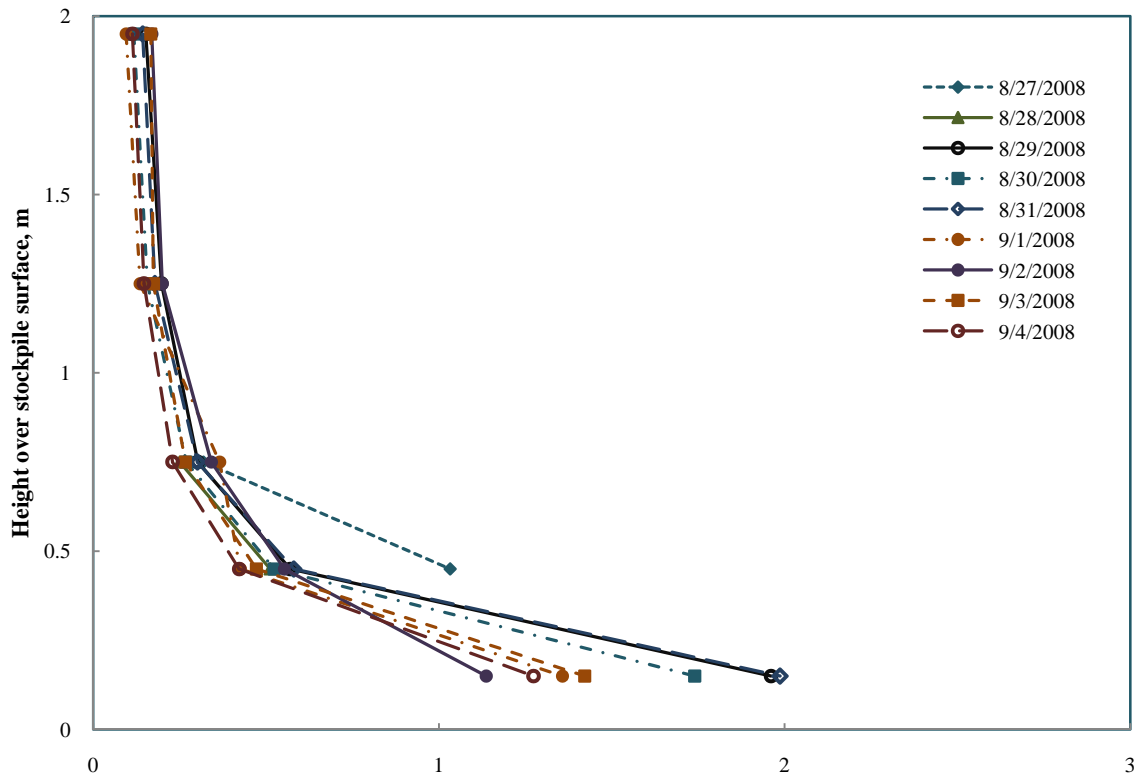
The slight difference in the profiles between summer and winter (Figure 4-2) may have been due to a number of different reasons. In winter, the stockpile was ~0.2 m higher than the stockpile in summer which probably modified the profile but should not have resulted in maximum wind speed at height of 0.75 m vs. 0.45 m in summer. Location of the lower chord of the trusses (1.2-m apart) with respect to the stockpiles edges could have affected the velocity profiles over the stockpiles differently in summer vs. winter. Finally, the predominant wind directions in summer and winter were somewhat different and these may have also affected the velocity profiles. Prevailing wind direction during the summer study was ESE (110-115°) whereas during winter study, it was SSW (200-205°) (Weather underground).

### 4.1.3 Ammonia concentration

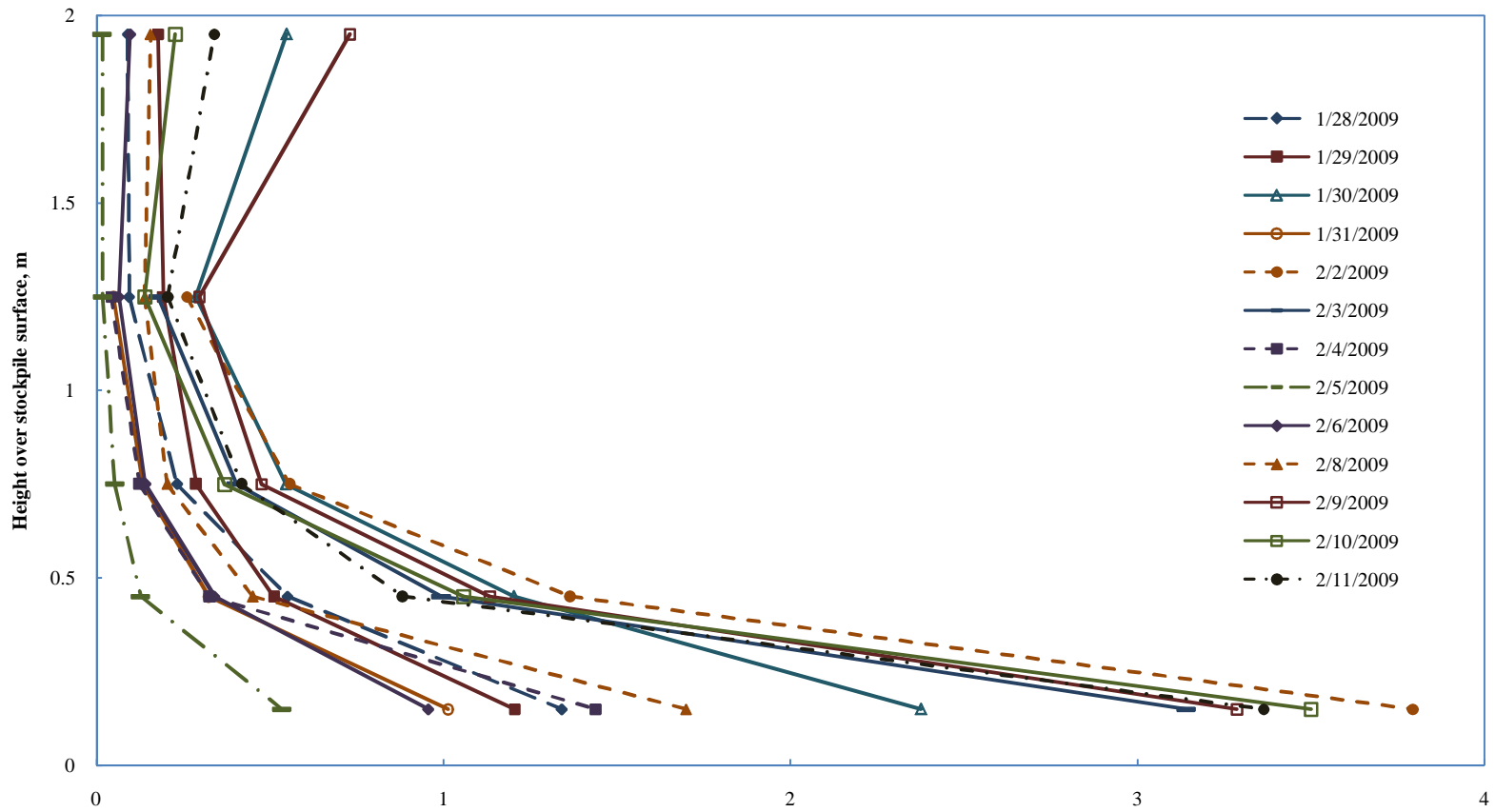
The measured ammonia concentration profiles are shown in Figure 4-3. The concentration profiles shown in Figure 4-3 (a) and (b) were due to forced convection while concentration profiles in Figure 4-3 (c) and (d) were due to natural convection. In summer, the ammonia concentration data at 0.15 m and 1.25 m was lost on 8/27/2008 and 8/28/2008 because of solenoid failure. In winter, data for

2/1/2009 was lost because the acid solutions in the scrubbers froze. During 1/31/2009 to 2/4/2009, the pump at 1.95 m height malfunctioned even though it was replaced every day. Subsequently addition of a moisture trap between the scrubber and pump prevented recurrence of the problem. Ammonia concentration on 2/7/2009 was discarded, because on that day the system only ran for 3.5 h (13:22-17:05).

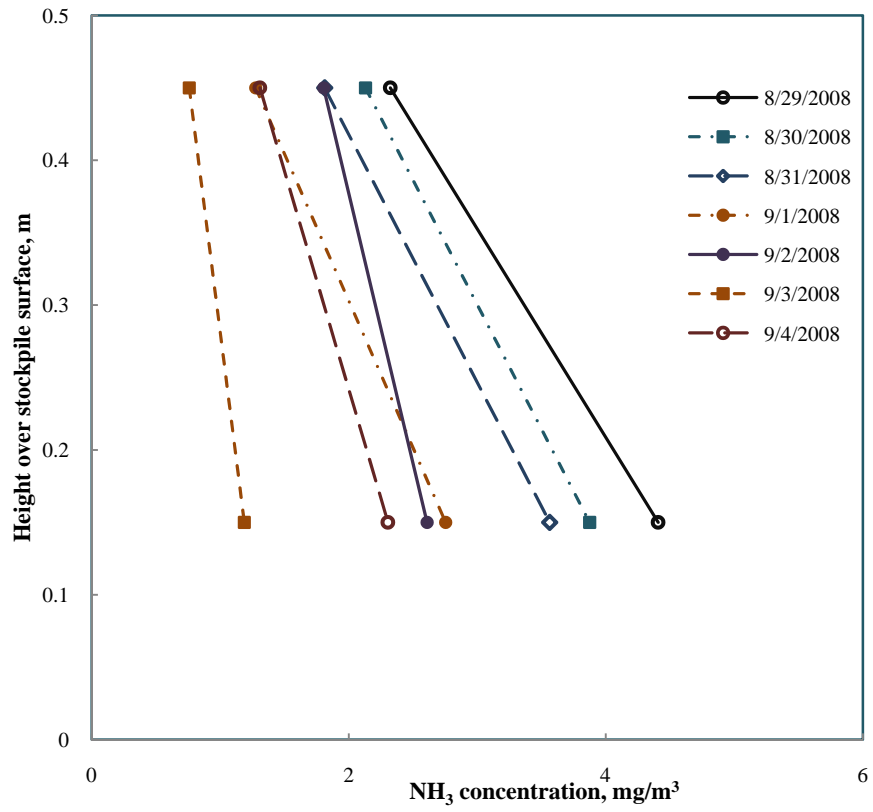
Figure 4-3 Ammonia concentration profiles in the (a) Summer (Forced), (b) Winter (Forced), (c) Summer (Natural) and (d) Winter (Natural) studies. The ammonia concentration data at 0.15 m and 1.25 m were lost on 8/27/2008 and 8/28/2008; hence, concentration data for natural convection for those 2 d are not presented. The ammonia concentration data for all heights except 0.15 m were lost on 2/1/2009; hence, forced convection concentrations are not presented for that day. The ammonia concentration data at 1.95 m was lost between 1/31/2009 and 2/4/2009. The ammonia concentration data at all heights were lost on 2/7/2009. Each data point is based on measurement for one scrubber. The adjacent data points for the same day are connected with lines to show trend



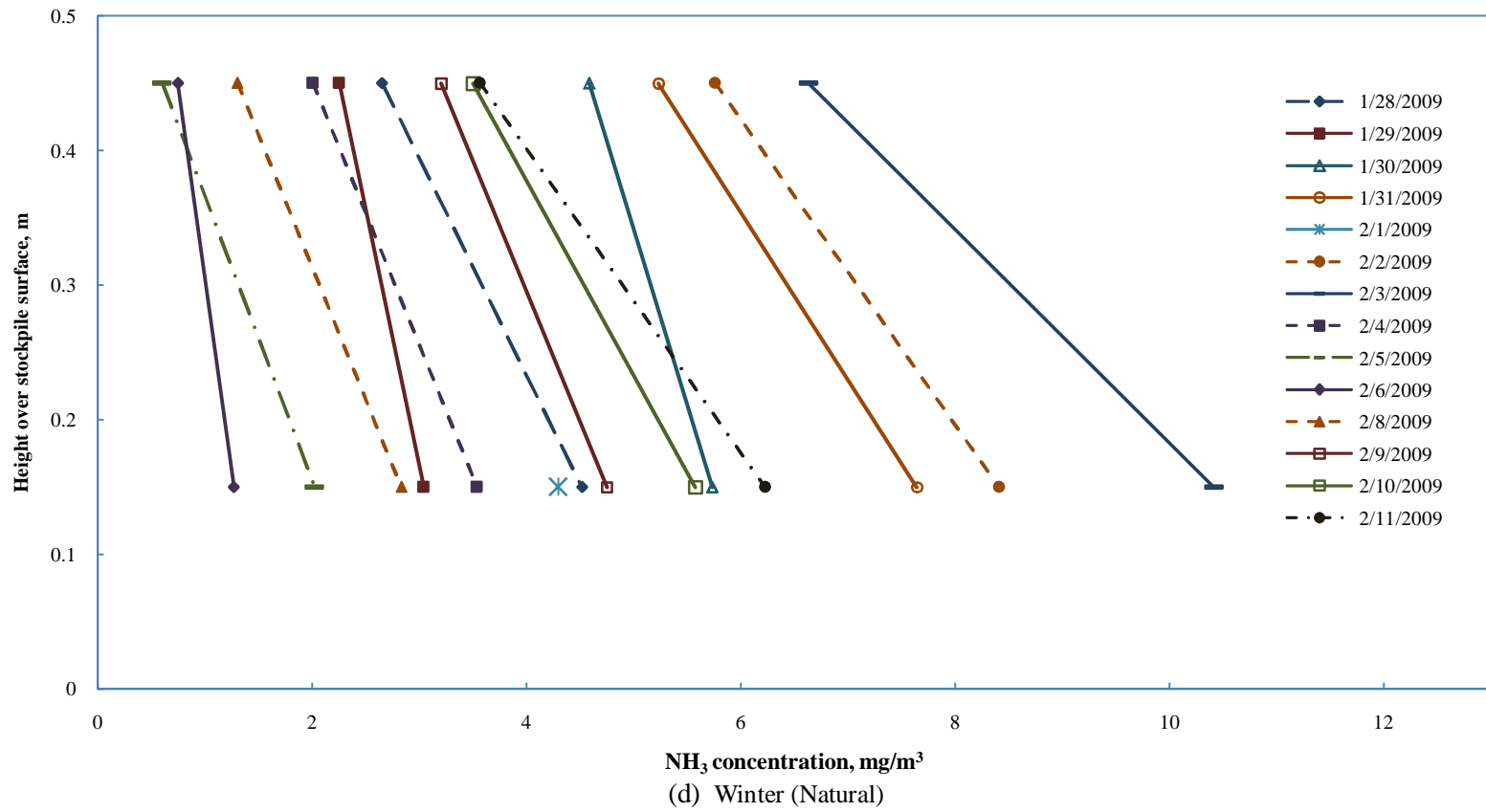
NH<sub>3</sub> concentration, mg/m<sup>3</sup>  
 (a) Summer (Forced)



NH<sub>3</sub> concentration, mg/m<sup>3</sup>  
 (b) Winter (Forced)



(c) Summer (Natural)



Ammonia concentration near the stockpile surface was higher than at other heights in both summer and winter. As the height increased, the ammonia concentration decreased. This type of concentration profile was observed on all days during both seasons, except for the forced convection data at 1.95 m on 1/30, 2/6, 2/9, 2/10 and 2/11/2009. On each of those five days, ammonia concentration at 1.95 m was higher than concentration at 1.25 m; however, the reason for this was unclear. The ammonia concentration profiles for forced convection in this study were similar to the ammonia concentration profiles over aerodynamically smooth surfaces (e.g., [Denmead, 1983](#)). However, no published ammonia concentration profiles over solid waste stockpile could be located in the literature.

The natural convection, ammonia concentration at 0.45 m on 8/27/2008 was very high ( $>30 \text{ mg/m}^3$ ) because the stockpile had been covered with tarpaulin for 22 d before the experiment began. By the next day (8/28/2009), ammonia concentration at 0.45 m had decreased to levels ( $\sim 2.4 \text{ mg/m}^3$ ) observed during the remainder of the study. The natural convection, data for 8/27 and 8/28/2008 are not shown in [Figure 4-3 \(c\)](#).

[Table 4-1](#) shows average ammonia concentration at each height for the whole study. From [Table 4-1](#), it is clear that for forced convection, the winter concentrations were higher than the summer concentrations at all heights except 1.25 m. For natural convection, the winter concentrations were higher at both heights than the summer concentrations. For natural convection, the data on 8/27/2008 and 8/28/2008 were excluded from the calculations in [Table 4-1](#).

On those days, when measured data were available for all five heights, it was observed that power trend line provided an excellent fit between ammonia concentration versus height, irrespective of temperature or wind conditions (data not presented). Hence, missing concentration data (for one or two heights) for forced convection on a particular day were estimated based on interpolation and/or

extrapolation of a power trend line fitted through the measured ammonia concentration data. Data for all heights on 2/1/2009 and 2/7/2009 were lost. The extrapolated and measured concentration data was shown in Figure 4-4.

**Table 4-1 Comparison of average daily ammonia concentration in summer and winter at different heights over the broiler cake stockpile**

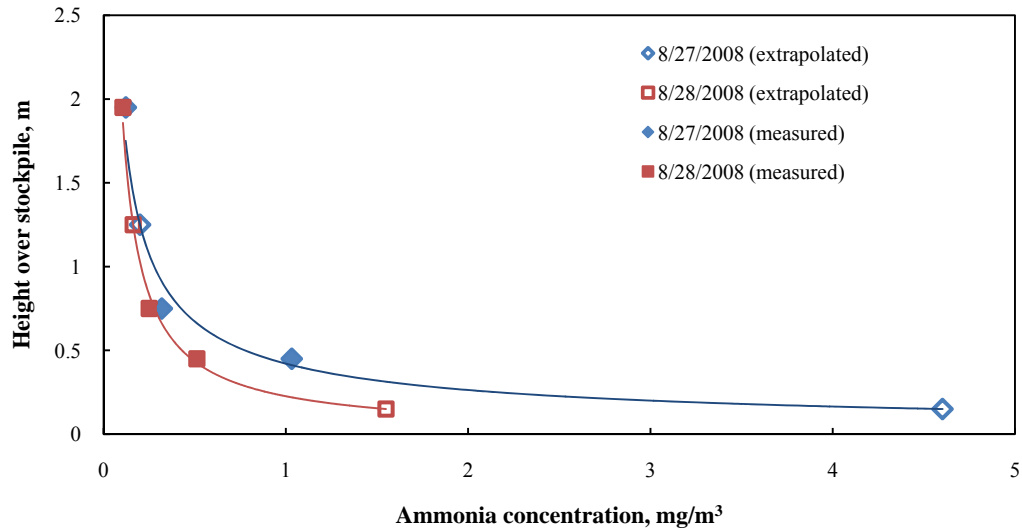
Height m	Ammonia concentration (Forced convection), mg/m <sup>3</sup>		Ammonia concentration (Natural convection), mg/m <sup>3</sup>	
	Summer <sup>a</sup>	Winter <sup>b</sup>	Summer <sup>a</sup>	Winter <sup>b</sup>
0.15	1.55	2.30	2.96 <sup>2</sup>	3.66
0.45	0.57	0.71	1.63	2.25
0.75	0.33	0.30		
1.25	0.19	0.15		
1.95	0.15	0.21 <sup>c</sup>		

<sup>a</sup> Data on 8/27 and 8/28/2008 was excluded from calculation.

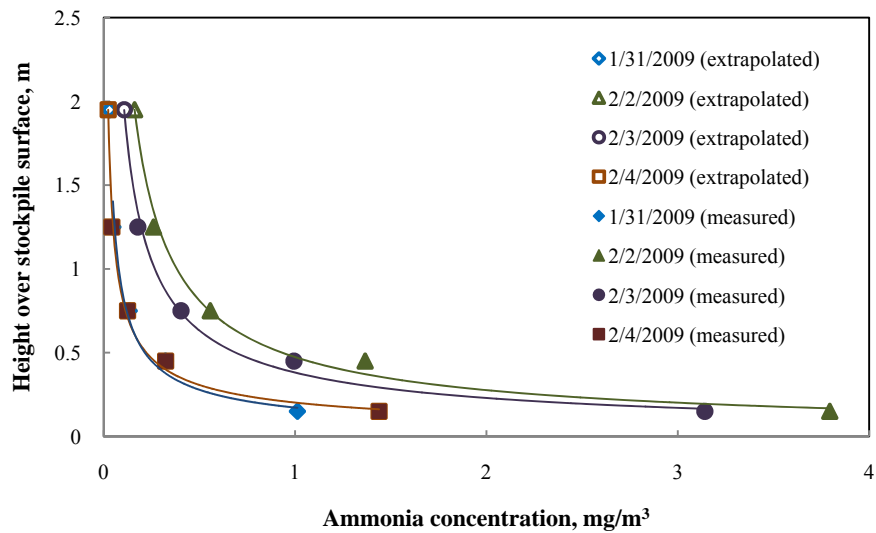
<sup>b</sup> Data on 2/1 and 2/7/2009 were lost for all heights.

<sup>c</sup> Includes extrapolated data for 1/31 to 2/4/2009.

Figure 4-4 Power trend lines used to estimate ammonia concentrations on those days when measured data were lost for one or two heights. Estimated concentrations are indicated using open symbols, while measured concentrations are indicated using solid symbols. The solid lines are concentration trend line (power) for each day.



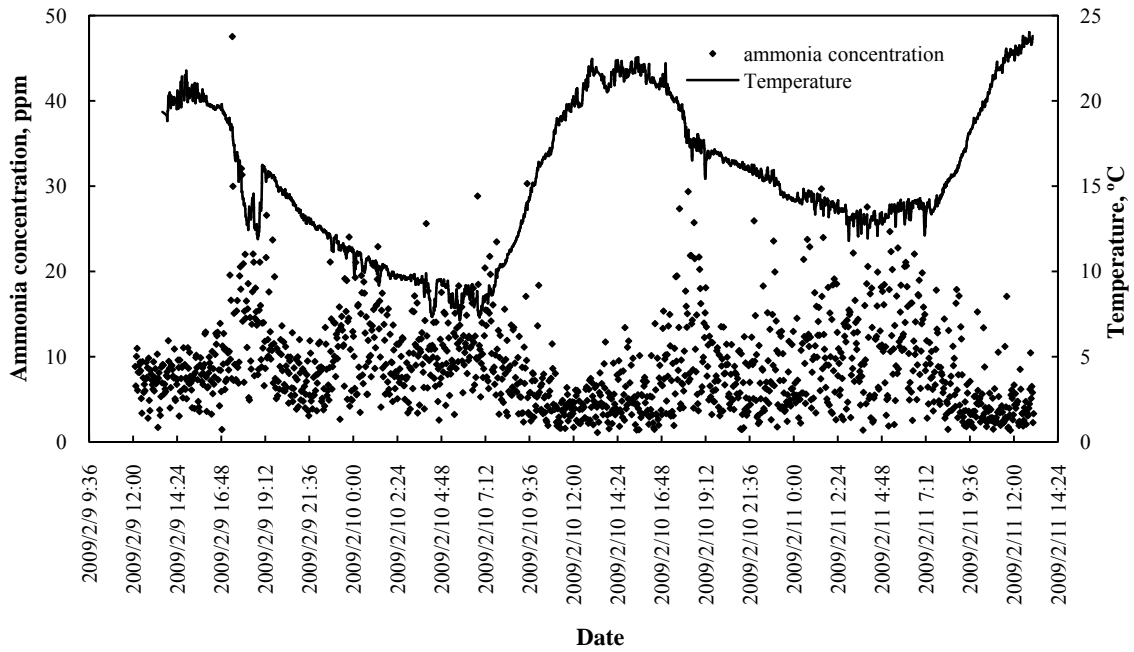
(a) Summer



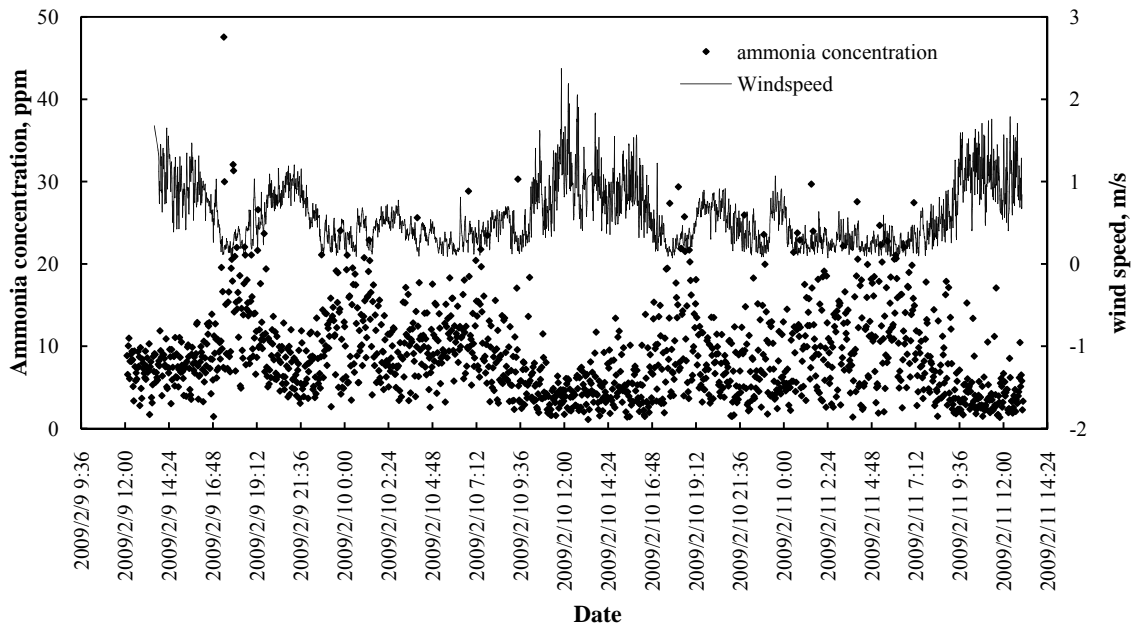
(b) Winter

Ammonia concentrations measured every 2 min at a height of 0.15 m above the stockpile surface with the photoacoustic sensor (INNOVA) during 2/9/2009 to 2/11/2009 are shown in Figure 4-5. The average ammonia concentration during these 2 d was 8.7 ppm (1.1 - 47.5 ppm) Ammonia concentrations generally decreased when the wind speed increased (Figure 4-5 (b)). As wind speed increased, it transported ammonia away from the stockpile surface, reducing its concentration on the

stockpile surface. Since wind speed and air temperature generally correlated with one-another, it seemed that ammonia concentration increased as temperature (and wind speed) decreased at night and early in the morning (Figure 4-5 (a)). The stockpile and air temperatures probably varied with some time lag; some difference in temperature between the stockpile and air could have also been due to the fact that there was microbial activity within the stockpile. Since ammonia production and release (from the stockpile) are affected by stockpile temperature, there is a need to measure stockpile temperature in future to directly assess the impact of stockpile temperature on ammonia emission.



(a) Ammonia concentration and air temperature (0.75 m above stockpile surface)



(b) Ammonia concentration and wind speed (0.75 m above stockpile surface)

Figure 4-5 Ammonia concentrations measured with the photoacoustic sensor at 2-min intervals over the broiler cake stockpile at 0.15-m height during the winter study.

#### 4.1.4 Occurrence of forced and natural convection conditions

The percentage of time of forced convection or natural convection (calculated based on  $Ri$  shown in eq. [3.8]) occurred over the stockpile, is shown in Table 4-2.

**Table 4-2 Occurrence of natural and forced convection conditions over the broiler cake stockpile surface in summer and winter**

		Natural convection (%)	Forced convection (%)	Average temperature (°C) <sup>a</sup>	Average wind speed 0.75 m above stockpile (m/s)
Summer	8/27/2008	0.44	95.51	24.06	1.32
	8/28/2008	0.97	87.73	25.28	0.86
	8/29/2008	1.55	85.89	26.62	0.46
	8/30/2008	1.03	90.24	26.10	0.55
	8/31/2008	1.48	85.50	26.87	0.48
	9/1/2008	2.10	83.67	25.61	0.64
	9/2/2008	3.43	83.35	22.93	0.50
	9/3/2008	3.21	85.94	22.66	0.45
	9/4/2008	1.42	88.06	24.13	0.56
		average	1.74	87.32	24.92
Winter	1/28/2009	1.22	91.88	12.33	1.02
	1/29/2009	6.80	80.31	12.75	0.86
	1/30/2009	16.11	73.07	6.19	0.46
	1/31/2009	4.25	93.42	5.27	1.61
	2/1/2009	10.56	78.79	5.94	0.81
	2/2/2009	8.05	81.16	8.99	0.59
	2/3/2009	4.10	90.17	8.32	1.24
	2/4/2009	6.87	88.46	3.72	1.44
	2/5/2009	0.94	98.24	-1.79	2.22
	2/6/2009	7.88	84.33	-1.39	0.81
	2/7/2009			System failure	
	2/8/2009	2.41	91.26	14.52	0.91
	2/9/2009	13.71	70.06	13.03	0.81
	2/10/2009	4.33	88.89	13.76	0.87
	2/11/2009	5.76	79.82	17.05	0.65
	average	6.64	84.99	8.48	1.02

<sup>a</sup> Average value of the temperatures monitored at 0.55 and 0.95 m above the stockpile

In summer, natural convection occurred 1.7% (range: 0.4 - 3.4%) of the time while forced convection occurred 87.3% (range: 83.4 – 95.5%) of the time; deposition conditions prevailed during

the remaining period. In winter, natural convection occurred 6.6% (range: 2.4 – 16.1%) of the time while forced convection occurred 85.0% (range: 70.0 – 98.2%) of the time.

Based on the t-test, natural convection occurred for significantly ( $p= 0.002$ ) longer percent of time (daily basis) in winter vs. summer. However, the summer and winter forced convection periods were not significantly different. Despite higher average wind speeds, natural convection was more prevalent during winter. It was likely that the temperature gradient ( $\Delta T$ ) above the stockpile used to compute Gr and hence Ri (eq. [3.4] and [3.8]) was larger and occurred for longer periods of time in winter than summer resulting in greater periods of natural convection in winter. However, as is clear from [Table 4-2](#), natural convection conditions occurred for longer periods of time when wind speeds were lower, the reverse was true for forced conditions. For example, with comparable air temperatures, natural convection conditions occurred eight times as long on 2/6/2009 than 2/5/2009 probably because wind speeds were much lower on 2/6/2009 ([Table 4-2](#)). It is unclear if the prevalence of natural vs. forced convections would have been different if the study had been conducted in an open area.

#### **4.1.5 Contribution of natural convection to total ammonia emission**

During both summer and winter, ammonia emissions due to forced convection represented >99.99% of the total ammonia emission (discussed in Chapter 4.1.6 below). Given that averaged daily ammonia concentrations due to natural convection were much higher than forced convection concentrations at the same heights ([Table 4-1](#)) and natural convection conditions occurred for up to 6.6% of the time ([Table 4-2](#)), the extremely low (<0.01%) contribution of natural convection to ammonia emission was unexpected. This is likely due to the fact that molecular diffusivity, even when assisted by rising warm air is much smaller in magnitude than turbulent diffusivity. Further, the natural

convection episodes were very short in duration (<5 s, data not presented), followed either by mixed or forced convection conditions.

Even though natural convection contributed little to the total ammonia emission in this study, if the ammonia concentration due to natural convection had been lumped with forced convection, ammonia concentration in the air would have been generally overestimated (Table 4-3). In Table 4-3, ‘natural convection lumped with forced’ was calculated by adding the masses in the forced and natural convection scrubbers and dividing the total mass by the sum of the volumes of air moved through those two scrubbers. From Table 4-3, it is evident that overestimation of ammonia concentration due to lumping increased (both heights) with increase in percent of natural time.

**Table 4-3 Ammonia concentrations due to forced convection only and when natural convection was also assumed to be part of forced convection for those heights (0.15 m and 0.45 m) for which data were available for both natural and forced convection conditions for selected days during the summer and winter studies**

Date	Percent of natural time	0.15 m			0.45 m		
		Forced concentration mg/m <sup>3</sup>	Natural convection lumped with forced mg/m <sup>3</sup>	Over estimate %	Forced concentration mg/m <sup>3</sup>	Natural convection lumped with forced mg/m <sup>3</sup>	Over estimate %
8/29/2008	1.55	1.96	2.00	2.21	0.57	0.60	5.01
8/30/2008	1.03	1.74	1.76	1.38	0.52	0.54	3.45
8/31/2008	1.48	1.99	1.73	-12.94	0.58	0.53	-8.92
2/8/2009	2.41	1.70	1.73	1.72	0.45	0.47	4.89
2/9/2009	13.71	3.29	3.53	7.29	1.13	1.47	29.92
2/10/2009	4.33	3.50	3.60	2.75	1.06	1.17	10.72
2/11/2009	5.76	3.36	3.56	5.73	0.88	1.06	20.47

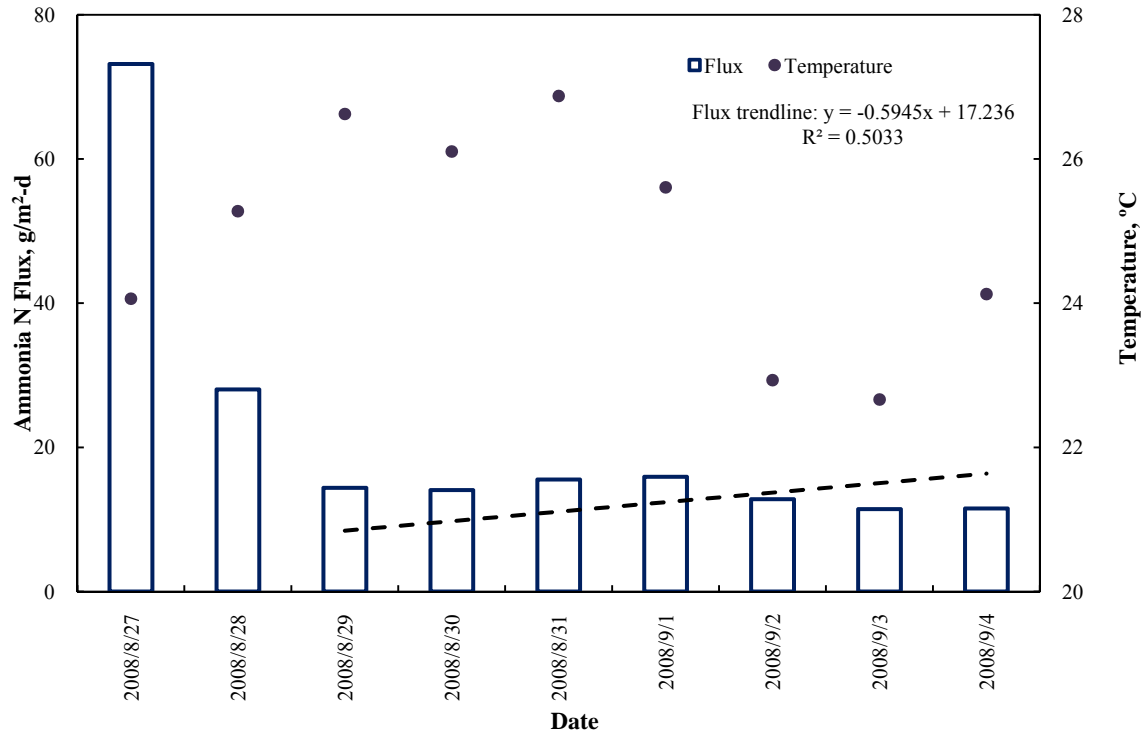
In all IHF studies reviewed, gas concentration measurement devices were operated without regard to convection conditions. Hence, based on this research (Table 4-3), not isolating gas concentrations during forced convection conditions may generally lead to overestimation of emissions. It also seems

that the magnitude of error would be higher under covered sheds during winter when natural conditions might occur for longer periods of time than summer.

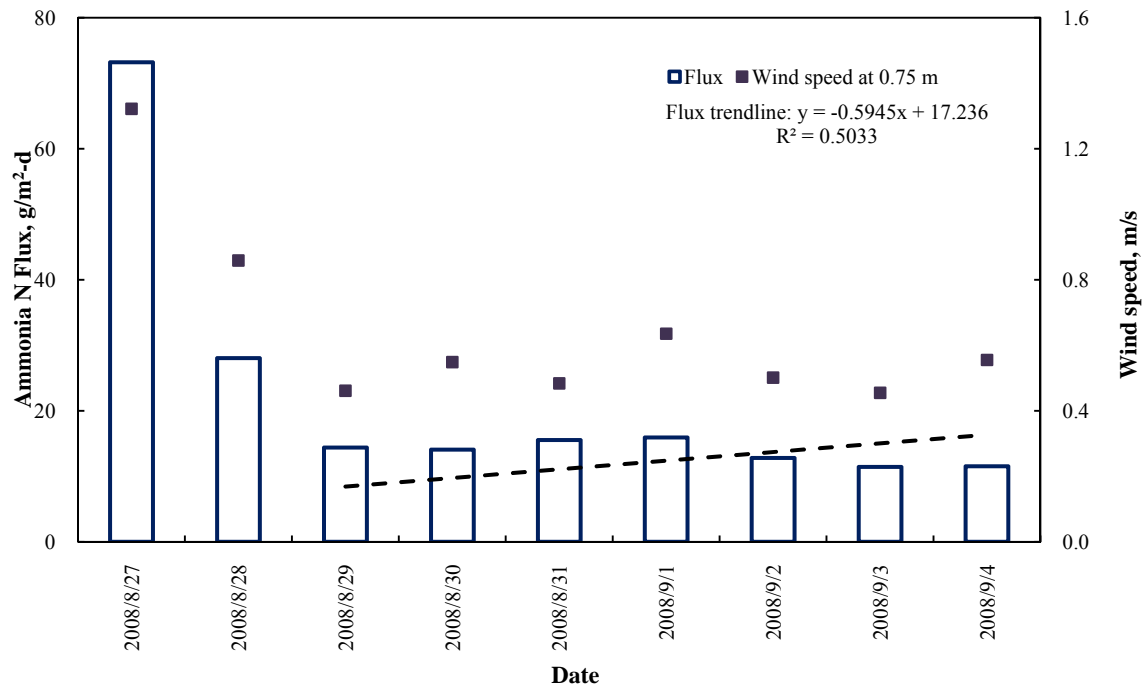
#### **4.1.6 Ammonia emission from broiler cake stockpile**

In summer, the ammonia flux [Figure 4-6 (a) & (b)] on 8/27/2008 and 8/28/2008 was estimated based on estimated concentration data (two heights) obtained by fitting a power trend line through the three measured concentration data points. In winter, the flux [Figure 4-6 (c) & (d)] from 1/31/2009 through 2/4/2009 was calculated based on extrapolated ammonia concentration data as the data for 1.95 m height was lost.

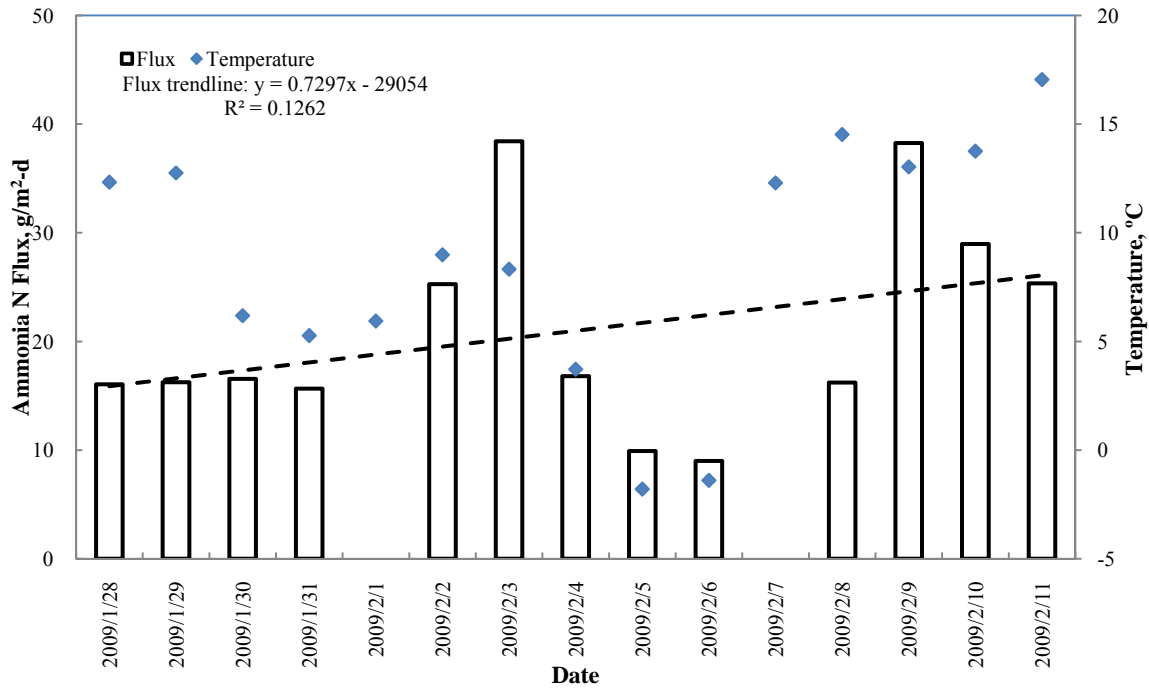
Figure 4-6 Ammonia N flux during summer and winter from the broiler cake stockpiles. Average daily wind speed was measured at 0.75 m height whereas average daily temperature was based on mean of measured data at 0.55 and 0.95 m. Area used for flux calculation included the top as well as the sides.



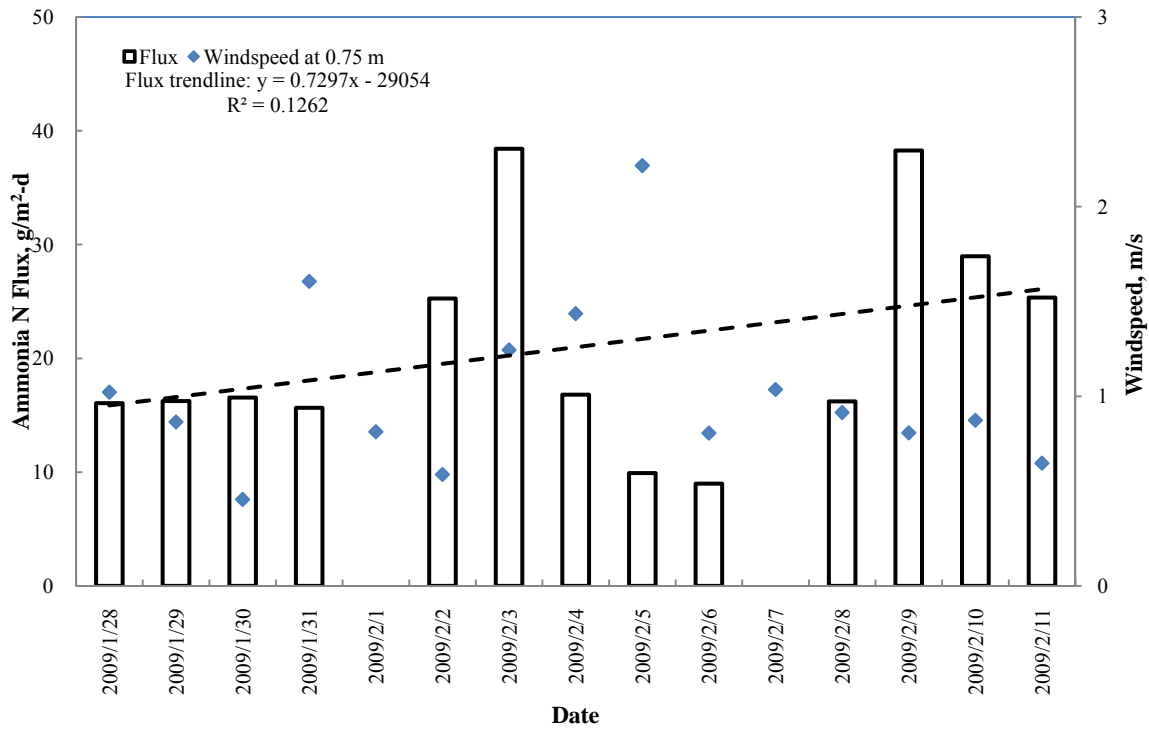
(a) Summer (with temperature)



(b) Summer (with wind speed)



(c) Winter (with temperature)



(d) Winter (with wind speed)

Ammonia flux was much higher on 8/27/2008 (Figure 4-6), the first day of the summer study. Because the stockpile had been covered with a tarp for the previous 22 d, it resulted in a spike of ammonia flux on 8/27/2008 (Figure 4-6 (a & b)). At the end of the second day of the study, ammonia flux in summer had been reduced by >50% compared with the previous day (Figure 4-6 (a & b)). In summer, the ammonia flux did not change much during the last 8 d of the study, irrespective of changes in the temperature and wind speed (Figure 4-6 (a-b)). In winter, compared with 1/29/2009, the ammonia flux increased slightly on 1/30/2009 when both temperature and wind speed decreased. Since ammonia flux increases with temperature, there was likely a substantial time lag between the air and stockpile temperatures. The emission on 2/3/2009 was much higher compared to 2/2/2009, because the wind speed more than doubled between 2/2 and 2/3/2009. During 2/3 through 2/5/2009, the reason of decreasing ammonia flux was due to decrease in air temperature even though the wind speed increased. Even though air temperature and wind speed declined slightly between 2/8 and 2/9/2009, ammonia emission on 2/9/2009 was >100% higher than 2/8/2009 probably due to the warming trend observed during 2/6 to 2/8/2009. This indicates that there may have been a 1 d lag between the air and stockpile temperatures. The reason for gradual decrease in ammonia flux from 2/9 through 2/11/2009 was not clear. It is possible that if monitoring had been conducted for a longer period of time daily emissions would have approached a steady state, as was observed in summer. From Figure 4-6, it is clear that both temperature and the wind speed played important roles in ammonia emission.

The ammonia-N fluxes and emission factors for the summer and winter stockpiles are shown in Table 4-4. The data for the first 2 d in summer (8/27/2008 and 8/28/2008) were excluded in calculating flux (Table 4-4). The specific surface area (volume basis) or the ratio of total surface area per unit volume of the summer and winter stockpiles were 1.79 and 1.61 m<sup>2</sup>/m<sup>3</sup>, respectively.

**Table 4-4 Ammonia-N fluxes and emission factors from the summer (1.79 m<sup>2</sup>/m<sup>3</sup>) and winter (1.61 m<sup>2</sup>/m<sup>3</sup>) broiler cake stockpiles**

(a) Total NH<sub>3</sub>-N emission

Period (d)	g/m <sup>2</sup> -area of stockpile		g/m <sup>3</sup> -volume of stockpile		g/kg total initial N in litter		g/AU <sup>a</sup>		
	Measured	Estimated	Measured	Estimated	Measured	Estimated	Measured	Estimated	
Summer <sup>b</sup>	7	96.7	96.7	171.6	171.6	8.4	8.4	49.33	49.33
Winter <sup>c</sup>	7	141.5	154.9	227.8	249.1	12.8	14.0	271.5	297.3
	15	269.2	272.7	433.4	439.1	24.4	24.7	516.5	523.3

(b) NH<sub>3</sub>-N emission factors

Period (d)	g/m <sup>2</sup> -d		g/m <sup>3</sup> -d		g/kg total initial N in litter-d		g/AU-d		
	Measured	Estimated	Measured	Estimated	Measured	Estimated	Measured	Estimated	
Summer	7	13.7	13.7	24.5	24.5	1.2	1.2	7.0	7.0
Winter	7	20.2	22.1	32.5	35.6	1.8	2.0	38.8	42.5
	15	20.7	21.0	33.4	33.8	1.9	1.9	39.7	40.2

<sup>a</sup> AU=500 kg live animal weight

<sup>b</sup> Estimated emissions for 8/27 and 8/28/2008 were excluded because they were not considered to be representative of stockpile emissions.

<sup>c</sup> Data for 2/1 and 2/7/2009 were lost for all heights. Emission for 1/31 through 2/4/2009 were calculated based on extrapolated concentration at 1.95 m height based on four measured values.

The ammonia-N emission factor based on stockpile surface area (top + sides), volume and initial N in winter were slightly higher than in summer for the same period (7 d) while the emission factor on AU basis (500 kg live animal weight) was much higher in winter (Table 4-4). Initial cake properties in summer vs. winter (Table 4-5) may have also influenced emissions, thus masking the weather effect. Despite lower TAN, higher pH in winter (Table 4-5) probably contributed to higher emission (area, volume, and initial N basis) in winter than in summer. Another reason for higher emission in winter may have been the higher wind speed vs. summer (Table 4-2). Ammonia emission factor on AU basis was much higher in winter than summer (Table 4-5), because much more cake was removed per AU in winter than in summer. In summer, an average (n=4) of 31,125 kg cake was removed from each house and the mass of birds removed was 81,194 kg/house. The stockpile was part of this removed cake. In winter, 103,140 kg of cake was removed from each house and the mass of the birds removed was 80,070 kg/house. Hence, using initial N concentration in the cake or litter as basis for comparing ammonia emission under different environmental conditions may be less subjective than the other

measures mentioned in Table 4-4. Reporting stockpile emissions based on specific surface area (volume basis) may allow for more meaningful comparison of emissions from stockpiles of different shapes and sizes.

**Table 4-5 Initial cake properties for the summer and winter cake stockpiles**

	TKN g/kg oven dry	TAN g/kg oven dry	NO <sub>3</sub> <sup>-</sup> /NO <sub>2</sub> <sup>-</sup> -N g/kg oven dry	pH	MC %
Summer <sup>a</sup> (n=3)	49.3±2.8 <sup>b</sup>	13.4±0.8	0.005±0.002	7.1±0.3	37.9±1.5
Winter (n=9)	52±5.2	8.1±1.6	0.4±0.5	8.2±0.2	36.6±2.7

<sup>a</sup> In summer, the samples were collected at the time of stockpiling, 22 d before the beginning of the study.

<sup>b</sup> Mean±SD

In this study, the total NH<sub>3</sub>-N loss was 96.7 g/m<sup>2</sup> during 7 d in summer, 154.9 g/m<sup>2</sup> during 7 d in winter and 272.7 g/m<sup>2</sup> during 15 d in winter (Table 4-4). The total NH<sub>3</sub>-N loss reported by Nicholson et al. (2004) was 42-572 g/m<sup>2</sup> from broiler litter during 6-12 months while it was 508-1111 g/m<sup>2</sup> from laying hen manure during 10-16 months. While the winter emission (272.7 g/m<sup>2</sup> over 15 d) in this study is in the mid-range of values reported by Nicholson et al. (2004) over 6-12 months for broiler litter, emissions may have been higher in this study if it had been continued for another month or two.

During the summer study, the total ammonia-N loss was 0.8 % of total N. In winter the total ammonia loss was 1.4 % in the first 7 d and 2.5 % of total N over the 15 d study (measured and estimated N losses were similar in winter). Rodhe et al. (2002) reported that cumulative ammonia-N loss was 7% of total N from an uncovered heap and 10% of total N from a covered heap over 7 months. Sagoo et al. (2007) reported cumulative ammonia-N loss of 19% from a roofed heap over 6 months. In this study, the average temperature was 24.9 °C (range: 22.7 – 26.9 °C) in summer and 8.5 °C (range: -1.4 – 17.0 °C) in winter, while the initial TAN of broiler cake was 13.4 g/kg oven dry in summer and 8.1 g/kg oven dry in winter. The temperature range for the study by Rodhe et al. (2002) was from -5 to 10 °C and the initial TAN of broiler manure was 6.7 g/kg. Despite lower TAN and temperatures than this study, the longer duration of study and higher initial moisture content (44.6% vs. 36.9 to 37.9% in this study) probably resulted in higher ammonia losses in the study by Rodhe et

al. (2002). Further, stockpiles used by Rodhe et al. (2002) probably received rainfall which may have increased ammonia losses.

#### 4.1.7 Nitrogen distribution inside the winter stockpile

There were nine samples (3 layers, 3 samples for each layer) collected at the beginning as well as the end of the 15-d study. The analyses of TKN, TAN,  $\text{NO}_3^-/\text{NO}_2^-$ -N, and pH at beginning and end of winter stockpiling are shown in Figure 4-7.

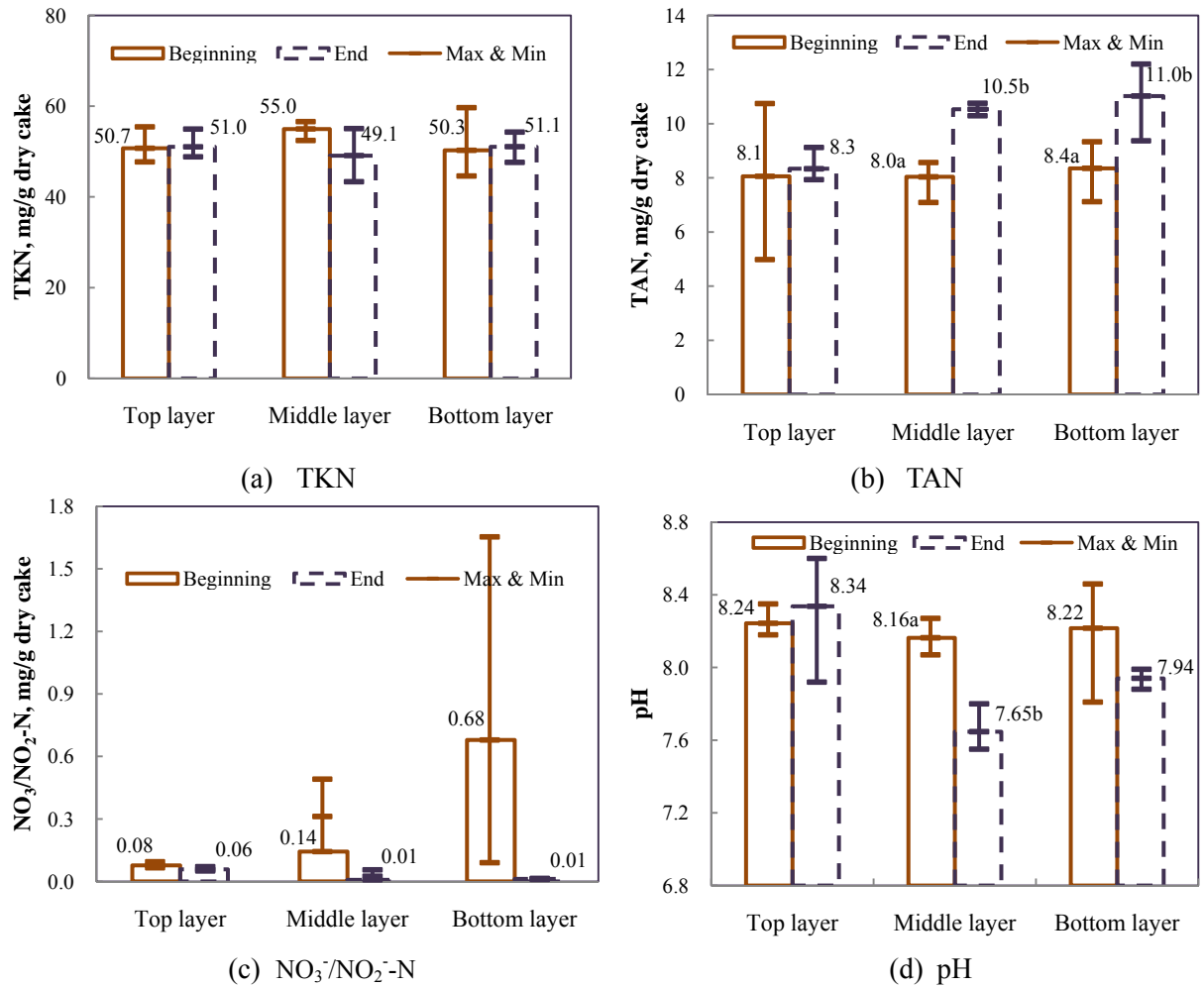


Figure 4-7 Comparison of (a) TKN (b) TAN (c)  $\text{NO}_3^-/\text{NO}_2^-$ -N and (d) pH in the winter stockpile at beginning and end of the study for each layer. Each value shown in the graph is the average of three replicates. The Max & Min are the maximum and minimum values of the three replicates. Top layer: 0-0.37 m; Middle layer: 0.37-0.74 m; Bottom layer: 0.74-1.1 m. Where shown, the alphabet following the average value indicates that the beginning and ending value were significantly different at  $\alpha=0.05$ .

Based on the t-test ( $\alpha=0.05$ ), the TKN concentration in each layer did not significantly change during the study. The TAN at the end was significantly higher than TAN at the beginning of the study for the middle and bottom layers (Figure 4-7 (b)). This indicated that in addition to some organic N mineralizing, the depth of the stockpile may have reduced  $\text{NH}_3$  escape from layers. As the TAN was only a small fraction of TKN, the before and after TKN were not significantly different (Figure 4-7 (a)) even though ammonia-N losses occurred from the stockpile. As for the top layer of the stockpile, there was no difference in TAN at the beginning and end indicating that the ammonia generation and loss rates were probably similar. Even at the beginning of the study, the  $\text{NO}_3^-/\text{NO}_2^-$ -N increased with depth (Figure 4-7 (c)) and the reason for this was unclear; however, the concentrations of  $\text{NO}_3^-/\text{NO}_2^-$ -N as compared to TKN were very small. The  $\text{NO}_3^-/\text{NO}_2^-$ -N concentrations decreased in the two lower layers (though not statistically) at the end of the study, indicating that denitrification likely happened inside the stockpile. Scarcity of  $\text{O}_2$  in the two lower layers likely caused denitrification and inhibited N mineralization beyond ammonification which can happen under low  $\text{O}_2$  conditions. However, since pH at the end of stockpiling was  $>6$  (Figure 4-7 (d)), denitrification would likely result in release of  $\text{N}_2$  (Tisdale *et al.*, 1993). Even as TAN increased in the middle and bottom layers, the pH decreased. This could be due to generation of  $\text{CO}_2$  (microbial respirations).

## 4.2 Chamber study

The chamber study was conducted for 13 d (11/11/2008 to 11/24/2008) at room temperature ( $23.7 \pm 0.7$  °C). The cake properties at the beginning and end of the experiment are shown in Table 4-6. The change in cake properties at the end of the study are discussed later.

**Table 4-6 Properties (n=9) of the cake used in the chamber study**

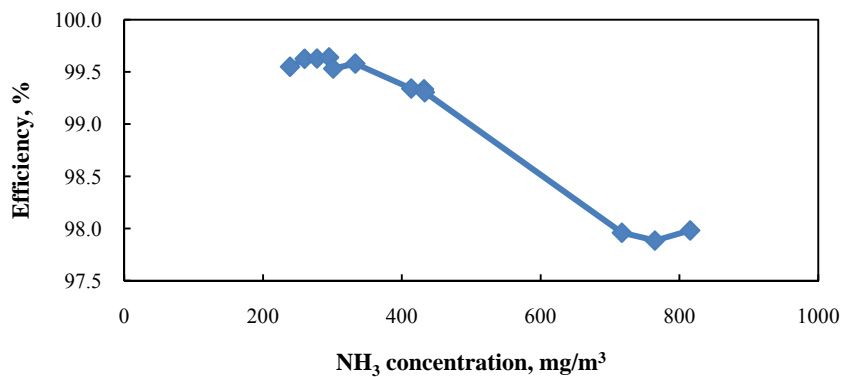
		TN	TAN	pH	MC
		g/kg oven dry	g/kg oven dry		%
Initial <sup>a</sup>		51.8±0.3	11.8±0.2	8.7±0.2	43.2±0.5
Final <sup>b</sup>	Control	41.7±0.4	6.1±0.3	8.6±0.1	36.4±0.8
	Treatment 1 (cover)	49.2±1.3	9.7±0.6	9.0±0.1	43.1±1.1
	Treatment 2 (double depth)	47.4±2.0	8.9±0.3	9.0±0.2	41.3±1.3

<sup>a</sup> Mean±SD of nine replicates

<sup>b</sup> Mean±SD of three replicates for each treatment

#### 4.2.1 Scrubber efficiency

During the first 3 d of study, scrubber efficiency was determined using eq. [3.14]. Based on 27 data points (3 d, 3 treatments, and 3 replicates per treatment) scrubber efficiency was in the range of ~98% to 99.6% when the ammonia concentration ranged from ~ 230 to 820 mg/m<sup>3</sup> at the outlet of the chamber (Figure 4-8). Even though scrubber efficiency was somewhat inversely correlated with ammonia concentration, even at high ammonia concentrations, the scrubber efficiency was very high. Such high efficiencies were observed probably because the study was conducted at room temperature (23.7 °C, range: 22.9 - 26.2 °C) and the system ran for 15 min on/45 min off. Because scrubber efficiency was very high, ammonia concentrations were not adjusted for scrubber efficiency while comparing the treatments.



**Figure 4-8 Scrubber efficiency based on NH<sub>3</sub> concentration at the outlet during 11/12 to 11/15/2008. Each data point represents one scrubber.**

#### 4.2.2 Ammonia concentration

For the 13-d study, the outlet ammonia concentration was calculated, based on air flow rate, duration, and mass of  $\text{NH}_3\text{-N}$ . [Figure 4-9](#) compares the ammonia concentrations from the three treatments over time.

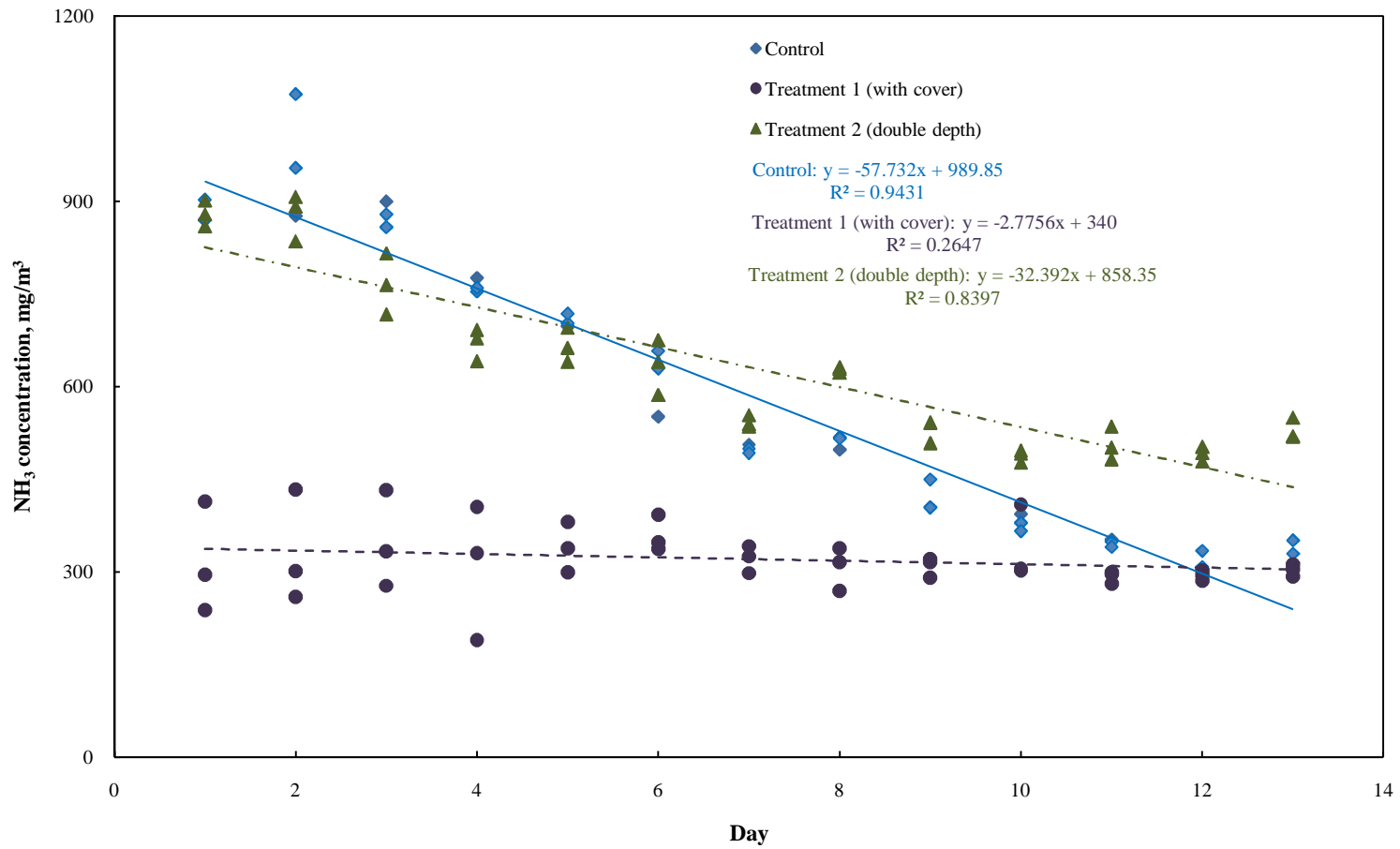


Figure 4-9 Change in ammonia concentration during the chamber study. Control is 70 mm of broiler cake with no cover. Treatment 1 is 70 mm of broiler cake covered by tarpaulin. Treatment 2 is 140 mm broiler cake with no cover. Each data point represents one scrubber.

For all three treatments, linear trend lines were used to characterize changes in ammonia concentration over time. [Figure 4-9](#) shows that the ammonia concentration in treatment 1 (70 mm broiler cake covered by tarpaulin) did not change with time and it was much lower than the other treatments. In the other two treatments (control and treatment 2), the ammonia concentration decreased over time. Earlier in the study, ammonia concentration in the control treatment (70 mm broiler cake without cover) was higher than treatment 2 (140 mm broiler cake without cover); however, later in the study, the trend reversed ([Figure 4-9](#)). The ammonia concentration in the control treatment decreased faster than treatment 2 as indicated by a greater negative slope. Because there was double the amount of broiler cake (hence, N) in treatment 2 than control treatment, reduction in ammonia concentration was lower in treatment 2. After 10 d, the ammonia concentration from the control treatment was similar to treatment 1 probably due to depletion of TAN.

In all three treatments, even at the end of the study, outlet ammonia concentration was still very high. The cake in this study had higher moisture (43.2%; range: 42.4% - 43.8%) and TAN (11.8 g/kg oven dry cake; range: 11.3 - 12.2 g/kg oven dry cake) contents than in the study by [Liu et al. \(2007\)](#). Hence, the ammonia concentration in this study was much higher than in the study by [Liu et al. \(2007\)](#) where the highest ammonia concentration was 450 ppm (313 mg/m<sup>3</sup> at 25 °C).

### **4.2.3 Relative ammonia emission**

Ammonia flux (g/m<sup>2</sup>-d) and emission (g/m<sup>3</sup>-d) was calculated based on 6 h of operation each day (15 min on /45 min off) for 13 d. Repeated measures ANOVA ([SAS, 2008](#)) applied to the three treatments showed that there were significant treatments effects (p<0.05) over time on the ammonia emission (both on surface and volume basis). SAS code and output are shown in Appendix B and the residue plots (to check for normal distribution) are shown in Appendix B: [Figure B-1](#) and [B-2](#). On surface basis, treatment 1 (cover) had significantly lower relative ammonia emission than the control

treatment and treatment 2 (double depth); however, there was no significant difference between the control treatment and treatment 2 (Table 4-7). On volume basis, the control treatment had significantly higher relative ammonia emission than treatment 1 (cover) and treatment 2 (double depth); however, there was no significant difference between treatment 1 (cover) and treatment 2 (double depth) (Table 4-7).

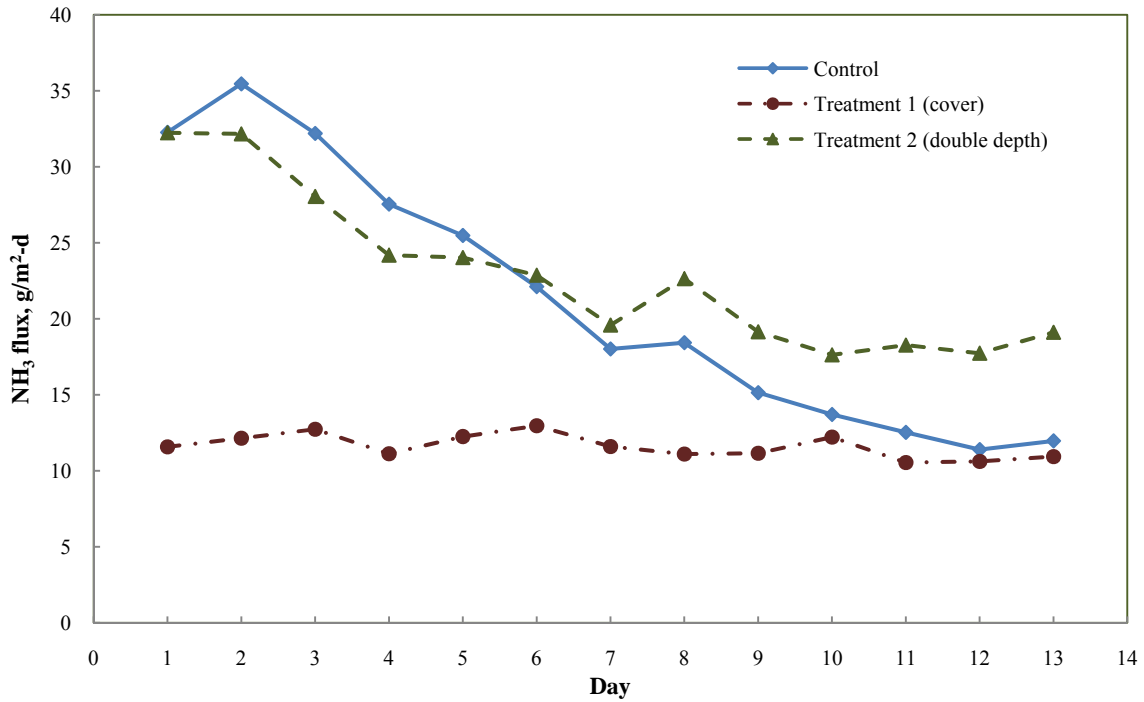
**Table 4-7 Least square means of the chamber treatments on surface area and volume bases**

Treatment <sup>a</sup>	Surface basis g/m <sup>2</sup> -d	Volume basis g/m <sup>3</sup> -d
Control treatment	21.2a <sup>b</sup>	303.6a
Treatment 1 (cover)	11.6b	165.8b
Treatment 2 (double depth)	22.9a	163.5b

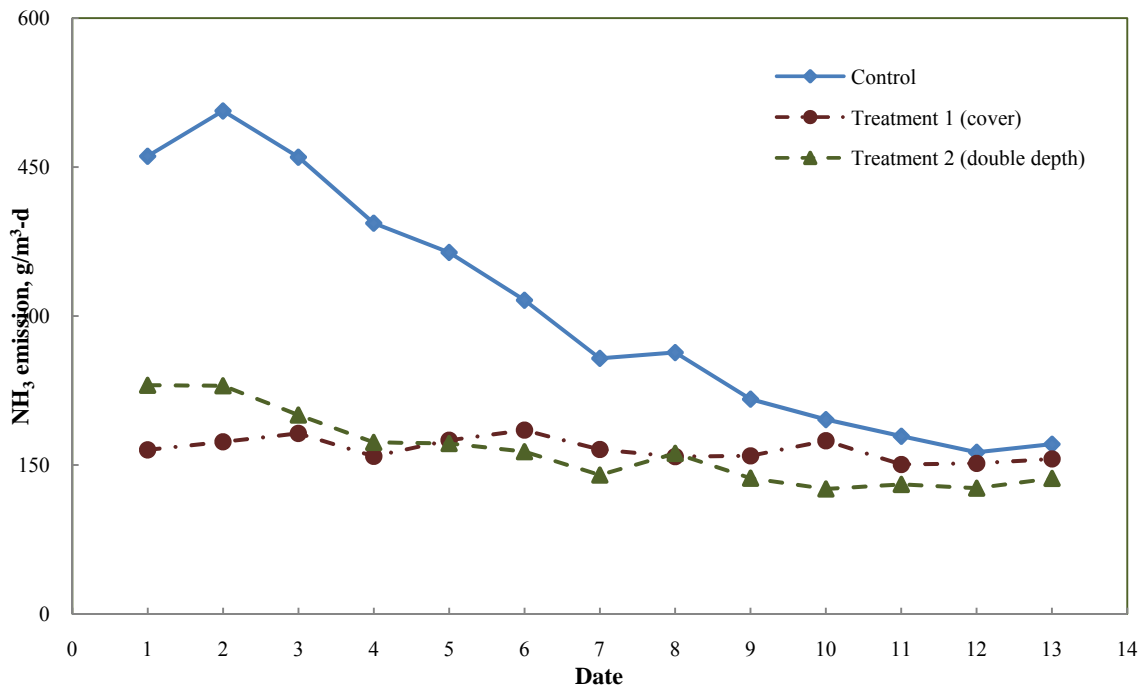
<sup>a</sup>Each treatment had three replications

<sup>b</sup>Mean values in the same column with the same alphabet are not significantly different at  $\alpha=0.05$ .

Changes in ammonia flux over time (Figure 4-10 (a)) were similar to changes in ammonia concentration (Figure 4-9) over time for all the treatments. Ammonia flux changed very little over time in treatment 1 (70 mm broiler cake covered with tarpaulin) (Figure 4-10 (a)). For the first 6 d, the ammonia flux from the control treatment (70 mm broiler cake without cover) was higher than treatment 2 (140 mm broiler cake without cover); thereafter, the trends were reversed. After 11 d, ammonia fluxes from the control treatment and treatment 1 were similar, probably due to depletion of TAN and reduced moisture content (Table 4-6) in the control treatment (Figure 4-10 (a)).



(a) Flux based on surface area



(b) Emission based on volume of broiler cake

Figure 4-10 Change in ammonia emission over time for the three treatments. Each data point is a mean of three replications.

On volume basis, ammonia emissions from treatment 1 and treatment 2 were similar to one-another and changed very little over time. By comparison, the control treatment had higher ammonia emission than the other two treatments in the beginning (Figure 4-10 (b)). Toward the end of the study, all three treatments had similar ammonia emission values (Figure 4-10 (b)) probably due to depletion of TAN and moisture in the control treatment.

Total ammonia fluxes for the entire study were 280.6, 151.7 and 303.2 g NH<sub>3</sub>/m<sup>2</sup> for the control, treatment 1 and treatment 2, respectively. The NH<sub>3</sub> lost for the first 7d and the whole study was compared using ANOVA (SAS, 2008) for the three treatments (Table 4-8).

**Table 4-8 Comparison of total relative ammonia emissions (a) based on surface area (b) based on volume of broiler cake from the three treatments (n=3) during the first 7 d and the whole period (13 d) ( $\alpha=0.05$ )**

(a) Ammonia lost per unit surface area				
	7 d		13 d	
	Mean NH <sub>3</sub> lost (SD) g/m <sup>2</sup>	MSD <sup>a</sup>	Mean NH <sub>3</sub> lost (SD) g/m <sup>2</sup>	MSD
Control	193.1(4.5) <sup>a</sup> <sup>b</sup>	25.7	276.2(5.3) <sup>a</sup>	27.2
Treatment 1	84.4(16.4) <sup>b</sup>		150.1(16.9) <sup>b</sup>	
Treatment 2	183.1(5.3) <sup>a</sup>		297.6(6.3) <sup>a</sup>	

(b) Ammonia lost based per unit volume				
	7 d		13 d	
	Mean NH <sub>3</sub> lost (SD) g/m <sup>3</sup>	MSD <sup>a</sup>	Mean NH <sub>3</sub> lost (SD) g/m <sup>3</sup>	MSD
Control	2758(64) <sup>a</sup> <sup>b</sup>	356	3946(76) <sup>a</sup>	372
Treatment 1	1205(234) <sup>b</sup>		2156(242) <sup>b</sup>	
Treatment 2	1308(38) <sup>b</sup>		2126(45) <sup>b</sup>	

<sup>a</sup> MSD: Minimum significant difference based on Tukey's honest significant difference

<sup>b</sup> Mean values in the same column with the same alphabet are not significantly different at  $\alpha=0.05$ .

Based on Tukey's HSD for the surface area basis, treatment 1 (tarp cover) had significantly lower relative ammonia emissions than control and treatment 2 (double depth) (Table 4-8). The control treatment was not significantly different than treatment 2 at 7 d or 13 d on surface area basis.

However, on per unit volume basis, the control treatment had significantly higher relative ammonia

emission than treatment 1 or treatment 2, while treatment 1 was not significantly different from treatment 2 at 7 d or 13 d.

The study showed that ammonia loss per unit surface area basis from covered cake was nearly half of that from broiler cake left uncovered, whereas the control and double depth were comparable for both durations ([Table 4-8](#)). However, ammonia losses on volume basis from covered and double depth were nearly half that from broiler cake left uncovered for both time durations ([Table 4-8](#)). Hence, this study showed that irrespective of the depth of the cake, ammonia emissions were comparable for the same surface area under the test conditions. Since treatment 2 had double the volume of cake than the control treatment, creating stockpiles with smaller surface area per unit volume could reduce emissions.

## 5 CONCLUSIONS AND RECOMMENDATION FOR FUTURE RESEARCH

In this study, a field experiment was conducted to develop ammonia emission factors for broiler cake stockpiles in summer and winter. A lab experiment was conducted to measure relative ammonia emissions as affected by type of cover and depth of cake. In the field study, scrubbers were used to measure ammonia concentration and the IHF method was used to measure ammonia emission from stockpiles. In the field, emissions due to natural and mechanical convections were separated. In the lab, ammonia concentrations were also measured with scrubbers. Key findings of the study are listed below.

1. Ammonia emissions due to natural convection was <0.01% of total emission and could be neglected. However, not isolating gas concentrations during forced convection conditions may generally lead to overestimation of emissions. So to accurately estimate emissions, it may be necessary to isolate ammonia concentrations during forced convection conditions, particularly under sheds in winter.
2. Ammonia concentrations measured with the photoacoustic sensor over a 2-d period was 8.7 ppm. Ammonia concentration generally increased as temperature and /or wind speed decreased. Since temperature and wind speed were positively correlated, it was unclear which of the two meteorological parameters had a bigger impact on ammonia concentrations. The stockpile and air temperature probably varied with some time lag.
3. In summer, the estimated total ammonia-N loss was 0.8 % of total N during 7 d. In winter, the total ammonia loss was 1.4 % of total N during the first 7 d and 2.5 % for the whole 15-d period.
4. The estimated ammonia loss in summer (7 d) was 171.6 g NH<sub>3</sub>-N/m<sup>3</sup> of cake or 49.3 g NH<sub>3</sub>-N/AU. The estimated total ammonia lost for the first 7 d in winter was 249.1 g

- $\text{NH}_3\text{-N}/\text{m}^3$  or 297.3 g  $\text{NH}_3\text{-N}/\text{AU}$ . The total ammonia lost for the 15-d winter study was 439.1 g  $\text{NH}_3\text{-N}/\text{m}^3$  or 523.3 g  $\text{NH}_3\text{-N}/\text{AU}$ .
5. The estimated average daily ammonia emission factor in summer (7 d) was 24.5 g  $\text{NH}_3\text{-N}/\text{m}^3\text{-d}$  of cake or 7.0 g  $\text{NH}_3\text{-N}/\text{AU-d}$ . The estimated daily ammonia emission factor for the first 7 d in winter was 35.6 g  $\text{NH}_3\text{-N}/\text{m}^3\text{-d}$  or 42.5 g  $\text{NH}_3\text{-N}/\text{AU-d}$ . The ammonia emission factor for the entire 15-d period of experiment in winter was 33.8 g  $\text{NH}_3\text{-N}/\text{m}^3\text{-d}$  or 40.2 g  $\text{NH}_3\text{-N}/\text{AU-d}$ .
  6. The scrubber efficiency was in the range of ~98% to 99.6% when the ammonia concentration ranged from ~ 230 to 820  $\text{mg}/\text{m}^3$ . It shows that even at high ammonia concentration, the scrubber efficiency was very high at 23.7 °C with a 25% duty cycle.
  7. Ammonia losses from the covered cake were significantly lower than the control and double depth treatments by 45% and 49%, respectively, at the end of study. Hence, covering stockpiles reduces ammonia loss during storage. Also, ammonia losses ( $\text{g}/\text{m}^3$ ) are lower from stockpiles with lower surface area per unit volume. Under the test conditions, when uncovered, ammonia emissions are proportional to the surface area.

Based on the results of this research, following are some recommendations for future study.

1. Based on the cake analysis in the winter study, it may be important to evaluate C/N ratio and oxygen concentration inside the stockpile. It may be necessary to simulate C and N transformations at different depths in the stockpile as affected by temperature and  $\text{O}_2$  availability to better simulate ammonia-N losses.
2. The temperature inside the stockpile should be measured to directly assess the impact of stockpile temperature on ammonia emission.

3. Ammonia emissions from uncovered and tarp-covered stockpiles should be compared in the field.

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## **APPENDICES**

## APPENDIX A CRbasic code for field study

Summer:

```
'Gill Windsonic Anemometers attached to Com2
'RMY Anemometers connected to C1
'Scrubber Control attached to C2

Const newLine = CHR(10)+CHR(13)
Const DataInt=3          'Time interval to average the collected data
Const DEGREE=35.87
Const WIDETH=4.7
Const LENGTH=6.5

Public anemomString As String * 43
Public anemomSubString(4) As String * 6
Public windSpeedVert
Public windSpeedHoriz(5)
Public windDirection
Public thermistorTemp(2)
Public cr1000Temp
Public loopCount
Public tempRecord(10)
Public sonicTemperature
dim numReturnedBytes
Public Direction
Public Direc
Public keniThermistor
Public tempThermistor
Public L
Public Re
Public Gr
Public deltaTemp
Public belta
Public GrtoRe
Public GrtoRe2
Public CountN
Public CountF
Public port7status
```

Public port8status

DataTable(windTab,True,-1)

  DataInterval(0,DataInt,sec,10)

  Average(1,windSpeedVert,FP2,0)

  Average(5,windSpeedHoriz,FP2,0)

  Average(1,Direction,FP2,0)

  Average(1,sonicTemperature,FP2,0)

  Average(2,thermistorTemp,FP2,0)

EndTable

DataTable(GrtoRe2,True,-1)

  DataInterval(0,3,sec,10)

  Sample(1,tempRecord,FP2)

  Sample(1,CountN,FP2)

  Sample(1,CountF,FP2)

  Sample(1,Direc,FP2)

  Sample(1,L,FP2)

  Sample(1,Gr,IEEE4)

  Sample(1,Re,IEEE4)

  Sample(1,GrtoRe,FP2)

EndTable

Sub pollGill(address, anemomNumber)

'address: ascii value of single character address of Anemometer

'anemomNumber: location in wind arrays to store to

  SerialFlush(Com2)

  SerialOut(Com2,CHR(address), "",0,10)

  SerialIn(anemomString,Com2,10,&h03,18)

  loopCount = 0

  If anemomString = "" Then

    Do

      SerialOut(Com2,"?", "",0,10)

      SerialOut(Com2,"?", "",0,10)

      SerialOut(Com2,"?", "",0,10)

      SerialOut(Com2,"?", "",0,10)

      SerialOut(Com2,CHR(address), "",0,10)

```

SerialIn(anemomString,Com2,10,&h03,18)
loopCount = loopCount + 1
Loop While anemomString = "" and loopCount < 5
EndIf
SplitStr(anemomSubString(1),anemomString,",",4,6)
windSpeedHoriz(anemomNumber)=anemomSubString(2)
' SerialOut(ComRS232,"Gill "+CHR(address)+" Polled - Replied:"+anemomString+newLine,"",0,0)
EndSub

```

```

Sub pollRMY3d(address, anemomNumber)
SerialFlush(Com3)
SerialOut(Com3,"M"+CHR(address)+"!", "", 0,0)
SerialIn(anemomString,Com3,-1,10,43)
windSpeedVert = Mid(anemomString,17,6)
windSpeedHoriz(anemomNumber)=Mid(anemomString,24,6)
windDirection=Mid(anemomString,31,5)
sonicTemperature =Mid(anemomString,37,7)
EndSub

```

```

Sub pollRMY2d(address, anemomNumber)
If address = 1 or address = 2 Then
If address = 1 Then
SDI12Recorder(anemomString,1,1,"R0!",1.0,0.0)
ElseIf address = 2
SDI12Recorder(anemomString,1,2,"R0!",1.0,0.0)
EndIf
SplitStr(anemomSubString(1),anemomString,"+",2,6)
windSpeedHoriz(anemomNumber)=anemomSubString(1)
EndIf
EndSub

```

```

'Convert the range of the wind direction from 0~360 to -180~180
Sub ChangeDirec()
Direction=windDirection+55

```

```

If Direction>360 Then
    Direction=Direction-360
EndIf
If Direction>180 and Direction<360 Then
    Direction=Direction-360
Endif
EndSub

Sub GrRe()
' Kinematic viscosity=-0.00000005*Temp*Temp*Temp+0.0001*Temp*Temp+0.0862*Temp+13.389
tempThermistor=(tempRecord(9)+tempRecord(10))/2
keniThermistor=-0.00000005*tempThermistor*tempThermistor*tempThermistor+0.0001*tempThermistor*tempThermistor+0.0862*tempThermistor+13.389
    keniThermistor=keniThermistor*0.000001
'tempRecord(7)--Average Direction every 2s
    Direc=ABS(tempRecord(7))
' Character Length
    If Direc>DEGREE and Direc<(180-DEGREE) Then
        L=(WIDTH/2)/sin(Direc*3.1416/180)
    Else
        L=abs((LENGTH/2)/cos(Direc*3.1416/180))
    Endif
' Renold's number

    Re=tempRecord(3)*L/keniThermistor
    deltaTemp=ABS(tempRecord(10)-tempRecord(9))
    belta=1/tempThermistor
' Grash of number
    Gr=9.81*belta*deltaTemp*L*L*L/(keniThermistor*keniThermistor)
    GrtoRe=Gr/(Re*Re)
EndSub

Sub SolinoidControl()
' C7 on && C8 on--Natural
' C7 on && C8 off--Forced
' C7 off && C8 off--False/Free air

```

```

'Free/False condition
" If windTab.windSpeedVert(1)>0 and windTab.windSpeedHoriz(3)=0 then
If tempRecord(1)>0 and tempRecord(4)=0 then
    portset(7,0)
    portset(8,0)
'Forced condition
Elseif tempRecord(1)>0 then
    portset(7,1)
    portset(8,0)
'Natural condition
Elseif tempRecord(1)=0 and tempRecord(4)=0 then
    portset(7,1)
    portset(8,1)
'Forced condition
Elseif tempRecord(1)=0
    portset(7,1)
    portset(8,0)
'Forced condition
Elseif tempRecord(1)<0 and GrtoRe<0.3 then
    portset(7,1)
    portset(8,0)
'Natural condition
Elseif tempRecord(1)<0 and GrtoRe>16 then
    portset (7,1)
    portset (8,1)
Endif
portget(port7status,7)
portget(port8status,8)
If port7status=1 and port8status=1 then
CountN=CountN+1
Elseif port7status=1 and port8status=0 then
CountF=CountF+1
Endif
EndSub

BeginProg

SerialOpen(Com2,38400,3,0,90)

```

```

SerialOpen(Com3,38400,3,0,90)
SerialOpen(ComRS232,115200,0,0,100)

CountN=0
CountF=0

Scan(1500,mSec,120,0)

    pollGill(ASCII("Q"),1)
    pollGill(ASCII("R"),2)
    pollRMY3d(ASCII("B"),3)
    pollRMY2d(2,4)
    pollRMY2d(1,5)

'ExciteV( ExChan, ExmV, Delay )
    ExciteV(VX1,2500,0)

'VoltDiff(thermistorTemp, Repts, Range, DiffChan, RevDiff, SettlingTime, Integ, Mult, Offset )
    VoltDiff(thermistorTemp(1),2,mV2500,1,1,0,250,0.071537,-72.78918)

ChangeDirec()
CallTable windTab
GetRecord(tempRecord, windTab,1)

If IfTime(0,3,sec) Then
    GrRe()
    CallTable GrtoRe2
    SolinoidControl()
Endif

NextScan
SerialClose(Com2)
SerialClose(Com3)
SerialClose(ComRS232)
EndProg

```

Winter:

```
'Gill Windsonic Anemometers attached to Com2
```

```

'RMY Anemometers connected to C1
'Scrubber Control attached to C2

Const newLine = CHR(10)+CHR(13)
Const DataInt=2      'Time interval to average the collected data    for winter: no average
Const DEGREE=35.87
Const WIDTH=4.7
Const LENGTH=6.5

Public anemomString As String * 43
Public anemomSubString(4) As String * 6
Public windSpeedVert
Public windSpeedHoriz(5)
Public windDirection
Public thermistorTemp(2)
Public cr1000Temp
Public loopCount
Public tempRecord(10)
Public sonicTemperature
dim numReturnedBytes
Public Direction
Public Direc
Public keniThermistor
Public tempThermistor
Public L
Public Re
Public Gr
Public deltaTemp
Public belta
Public GrtoRe
Public GrtoRe2
Public CountN
Public CountF
Public port7status
Public port8status

DataInterval(0,DataInt,sec,10)
sample(1,windSpeedVert,FP2,0)

```

```

sample(5,windSpeedHoriz,FP2,0)
sample(1,Direction,FP2,0)
sample(1,sonicTemperature,FP2,0)
sample(2,thermistorTemp,FP2,0)

```

EndTable

```
DataTable(GrtoRe2,True,-1)
```

```

DataInterval(0,2,sec,10)
Sample(1,tempRecord,FP2)
Sample(1,CountN,IEEE4)
Sample(1,CountF,IEEE4)
Sample(1,Direc,FP2)
Sample(1,L,FP2)
Sample(1,Gr,IEEE4)
Sample(1,Re,IEEE4)
Sample(1,GrtoRe,FP2)

```

EndTable

```
Sub pollGill(address, anemomNumber)
```

'address: ascii value of single character address of Anemometer

'anemomNumber: location in wind arrays to store to

```

SerialFlush(Com2)
SerialOut(Com2,CHR(address), "",0,10)
SerialIn(anemomString,Com2,10,&h03,18)
loopCount = 0
If anemomString = "" Then
  Do
    '
    SerialOut(ComRS232,"Calling Gill "+CHR(address)+newline,"",0,0)
    SerialOut(Com2,"?", "",0,10)
    SerialOut(Com2,"?", "",0,10)
    SerialOut(Com2,"?", "",0,10)
    SerialOut(Com2,"?", "",0,10)
    SerialOut(Com2,CHR(address),"",0,10)
    SerialIn(anemomString,Com2,10,&h03,18)
    loopCount = loopCount + 1
  Loop While anemomString = "" and loopCount < 5
EndIf

```

```

SplitStr(anemomSubString(1),anemomString,"",4,6)
windSpeedHoriz(anemomNumber)=anemomSubString(2)
' SerialOut(ComRS232,"Gill "+CHR(address)+" Polled - Replied:"+anemomString+newLine,"",0,0)
EndSub

```

```

Sub pollRMY3d(address, anemomNumber)
SerialFlush(Com3)
SerialOut(Com3,"M"+CHR(address)+"!", "",0,0)
SerialIn(anemomString,Com3,-1,10,43)
windSpeedVert = Mid(anemomString,17,6)
windSpeedHoriz(anemomNumber)=Mid(anemomString,24,6)
windDirection=Mid(anemomString,31,5)
sonicTemperature =Mid(anemomString,37,7)
EndSub

```

```

Sub pollRMY2d(address, anemomNumber)
If address = 1 or address = 2 Then
If address = 1 Then
SDI12Recorder(anemomString,1,1,"R0!",1.0,0.0)
ElseIf address = 2
SDI12Recorder(anemomString,1,2,"R0!",1.0,0.0)
EndIf
SplitStr(anemomSubString(1),anemomString,"+",2,6)
windSpeedHoriz(anemomNumber)=anemomSubString(1)
EndIf
EndSub

```

'Convert the range of the wind direction from 0~360 to -180~180 for winter the range is from 0~360

```

Sub ChangeDirec()
'Direction=windTab.windDirection(1,1)+55
Direction=windDirection+55

If Direction>180
Direction=Direction-360
EndIf

```

```
EndSub
```

```
Sub GrRe()
```

```
' Kinematic viscosity=-0.0000005*Temp*Temp*Temp+0.0001*Temp*Temp+0.0862*Temp+13.389
```

```
tempThermistor=(tempRecord(9)+tempRecord(10))/2
```

```
keniThermistor=-0.0000005*tempThermistor*tempThermistor*tempThermistor+0.0001*tempThermistor*tempThermistor+0.0862*tempThermistor+13.389
```

```
keniThermistor=keniThermistor*0.000001
```

```
'tempRecord(7)--Average Direction every 2s
```

```
Direc=ABS(tempRecord(7))
```

```
' Character Length
```

```
If Direc>DEGREE and Direc<(180-DEGREE) Then
```

```
L=(WIDTH/2)/sin(Direc*3.1416/180)
```

```
Else
```

```
L=abs((LENGTH/2)/cos(Direc*3.1416/180))
```

```
Endif
```

```
' Renold's number
```

```
Re=tempRecord(3)*L/keniThermistor
```

```
deltaTemp=ABS(tempRecord(10)-tempRecord(9))
```

```
belta=1/tempThermistor
```

```
' Grash of number
```

```
Gr=9.81*belta*deltaTemp*L*L*L/(keniThermistor*keniThermistor)
```

```
GrtoRe=Gr/(Re*Re)
```

```
EndSub
```

```
Sub SolinoidControl()
```

```
' C7 on && C8 on--Natural
```

```
' C7 on && C8 off--Forced
```

```
' C7 off && C8 off--False/Free air
```

```
'Free/False condition
```

```
If tempRecord(1)>0 and tempRecord(4)=0 then
```

```
portset(7,0)
```

```
portset(8,0)
```

```
'Forced condition
```

```
Elseif tempRecord(1)>0 then
```

```

    portset(7,1)
    portset(8,0)
'Natural condition
Elseif tempRecord(1)=0 and tempRecord(4)=0 then
    portset(7,1)
    portset(8,1)
'Forced condition
Elseif tempRecord(1)=0
    portset(7,1)
    portset(8,0)
'Forced condition
Elseif tempRecord(1)<0 and GrtoRe<0.3 then
    portset(7,1)
    portset(8,0)
'Natural condition
Elseif tempRecord(1)<0 and GrtoRe>16 then
    portset (7,1)
    portset (8,1)
Endif
portget(port7status,7)
portget(port8status,8)
If port7status=1 and port8status=1 then
CountN=CountN+1
Elseif port7status=1 and port8status=0 then
CountF=CountF+1
Endif
EndSub

BeginProg

SerialOpen(Com2,38400,3,0,90)
SerialOpen(Com3,38400,3,0,90)
SerialOpen(ComRS232,115200,0,0,100)

CountN=0
CountF=0

Scan(2000,mSec,120,0)

```

```

pollGill(ASCII("Q"),1)
pollGill(ASCII("R"),2)
pollRMY3d(ASCII("B"),3)
pollRMY2d(2,4)
pollRMY2d(1,5)

'ExciteV( ExChan, ExmV, Delay )
  ExciteV(VX1,2500,0)

'VoltDiff(thermistorTemp, Repts, Range, DiffChan, RevDiff, SettlingTime, Integ, Mult, Offset )
  VoltDiff(thermistorTemp(1),2,mV2500,1,1,0,250,0.071537,-72.78918)

ChangeDirec()
CallTable windTab
GetRecord(tempRecord, windTab,1)

If IfTime(0,2,sec) Then
  GrRe()
  CallTable GrtoRe2
  SolinoidControl()
Endif

NextScan
SerialClose(Com2)
SerialClose(Com3)
SerialClose(ComRS232)
EndProg

```

## APPENDIX B Chamber study

residual plot for diagnostics

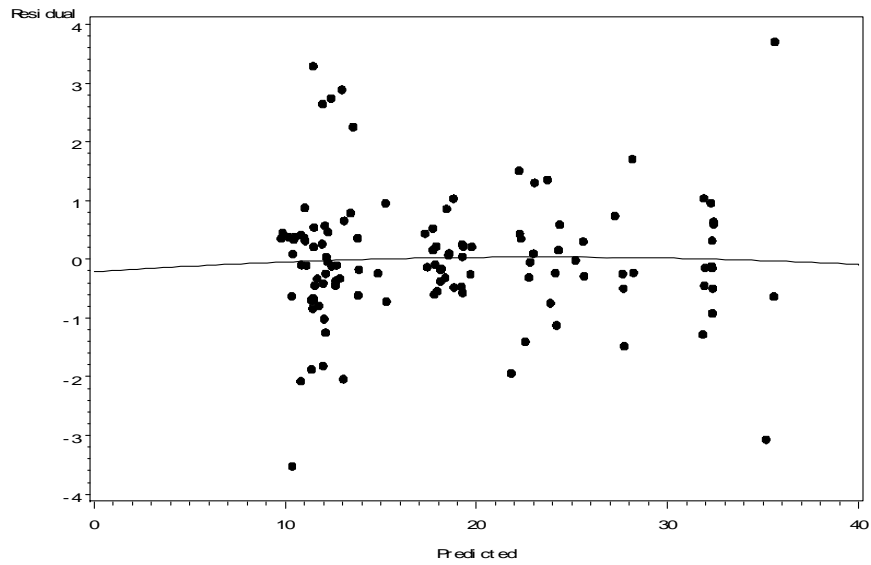


Figure B-0-1 Residual plot for diagnostics based on treatment and date effect (flux based on the surface area)

residual plot for diagnostics

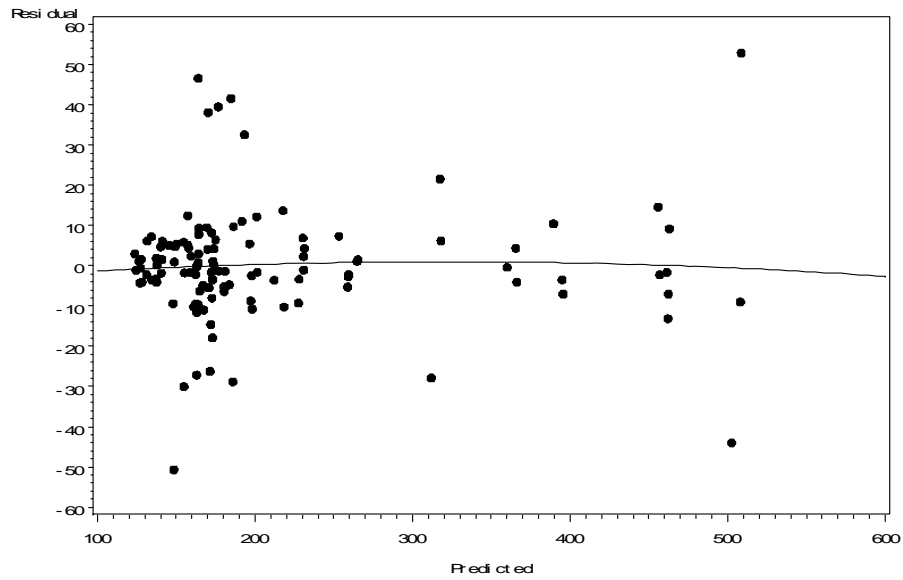


Figure B-0-2 Residual plot for diagnostics based on treatment and date effect (flux based on the volume of the cake)

## Ammonia flux over time

SAS code

```
proc mixed data=chamberflux;
  title "autoregressive";
  class Date Trt Bucket;
  model Flux=Date|Trt/ solution outp=residue;
  random Bucket;
  repeated Date / subject= Bucket type=ar(1);
  LSMeans Trt/ADJUST=TUKEY;

run;
```

SAS output

Flux based on the surface area:

autoregressive		
The Mixed Procedure		
Model Information		
Data Set	WORK.CHAMBERFLUX	
Dependent Variable	Flux	
Covariance Structures	Variance Components, Autoregressive	
Subject Effect	Bucket	
Estimation Method	REML	
Residual Variance Method	Profile	
Fixed Effects SE Method	Model-Based	
Degrees of Freedom Method	Containment	
Class Level Information		
Class	Levels	Values

Date	13	12NOV2008	13NOV2008	14NOV2008
		15NOV2008	16NOV2008	17NOV2008
		18NOV2008	19NOV2008	20NOV2008
		21NOV2008	22NOV2008	23NOV2008
		24NOV2008		
Trt	3	1	2	3
Bucket	9	1	2	3
		4	5	6
		7	8	9

Dimensions

Covariance Parameters	3
Columns in X	56
Columns in Z	9
Subjects	1
Max Obs Per Subject	117

Number of Observations

Number of Observations Read	117
Number of Observations Used	117
Number of Observations Not Used	0

Iteration History

Iteration	Evaluations	-2 Res Log Like	Criterion
0	1	329.00208613	
1	3	307.55402519	0.00000058
2	1	307.55397766	0.00000000

\*\*\*\*\*

autoregressive

The Mixed Procedure

Convergence criteria met.

Covariance Parameter Estimates

Cov Parm	Subject	Estimate
Bucket		0.4270
AR(1)	Bucket	0.3763
Residual		1.8725

Fit Statistics

-2 Res Log Likelihood	307.6
AIC (smaller is better)	313.6
AICC (smaller is better)	313.9
BIC (smaller is better)	314.1

Solution for Fixed Effects

Effect	Date	Trt	Estimate	Standard Error	DF	t Value	Pr >  t
Intercept			19.1084	0.8755	6	21.83	<.0001
Date	12NOV08		13.1291	1.1173	72	11.75	<.0001
Date	13NOV08		13.0569	1.1173	72	11.69	<.0001
Date	14NOV08		8.9432	1.1173	72	8.00	<.0001
Date	15NOV08		5.0791	1.1172	72	4.55	<.0001
Date	16NOV08		4.9188	1.1171	72	4.40	<.0001
Date	17NOV08		3.7621	1.1167	72	3.37	0.0012
Date	18NOV08		0.4753	1.1157	72	0.43	0.6714
Date	19NOV08		3.5331	1.1131	72	3.17	0.0022
Date	20NOV08		0.03436	1.1060	72	0.03	0.9753
Date	21NOV08		-1.4831	1.0871	72	-1.36	0.1767

Date	22NOV08		-0.8418	1.0352	72	-0.81	0.4188
Date	23NOV08		-1.3743	0.8824	72	-1.56	0.1237
Date	24NOV08		0	.	.	.	.
Trt		1	-7.1406	1.2382	72	-5.77	<.0001
Trt		2	-8.1770	1.2382	72	-6.60	<.0001
Trt		3	0	.	.	.	.
Date*Trt	12NOV08	1	7.1669	1.5801	72	4.54	<.0001
Date*Trt	12NOV08	2	-12.4913	1.5801	72	-7.91	<.0001
Date*Trt	12NOV08	3	0	.	.	.	.
Date*Trt	13NOV08	1	10.4332	1.5801	72	6.60	<.0001
Date*Trt	13NOV08	2	-11.8515	1.5801	72	-7.50	<.0001
Date*Trt	13NOV08	3	0	.	.	.	.
Date*Trt	14NOV08	1	11.2858	1.5801	72	7.14	<.0001
Date*Trt	14NOV08	2	-7.1433	1.5801	72	-4.52	<.0001
Date*Trt	14NOV08	3	0	.	.	.	.

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autoregressive

The Mixed Procedure

Solution for Fixed Effects

Effect	Date	Trt	Standard		DF	t Value	Pr >  t
			Estimate	Error			
Date*Trt	15NOV08	1	10.4961	1.5800	72	6.64	<.0001
Date*Trt	15NOV08	2	-4.8902	1.5800	72	-3.10	0.0028
Date*Trt	15NOV08	3	0	.	.	.	.
Date*Trt	16NOV08	1	8.5950	1.5798	72	5.44	<.0001
Date*Trt	16NOV08	2	-3.6018	1.5798	72	-2.28	0.0256
Date*Trt	16NOV08	3	0	.	.	.	.
Date*Trt	17NOV08	1	6.3847	1.5793	72	4.04	0.0001
Date*Trt	17NOV08	2	-1.7350	1.5793	72	-1.10	0.2756
Date*Trt	17NOV08	3	0	.	.	.	.
Date*Trt	18NOV08	1	5.5716	1.5779	72	3.53	0.0007
Date*Trt	18NOV08	2	0.1890	1.5779	72	0.12	0.9050

Date*Trt	18NOV08	3	0	.	.	.	.
Date*Trt	19NOV08	1	2.9261	1.5741	72	1.86	0.0671
Date*Trt	19NOV08	2	-3.3670	1.5741	72	-2.14	0.0358
Date*Trt	19NOV08	3	0	.	.	.	.
Date*Trt	20NOV08	1	3.1380	1.5642	72	2.01	0.0486
Date*Trt	20NOV08	2	0.1832	1.5642	72	0.12	0.9071
Date*Trt	20NOV08	3	0	.	.	.	.
Date*Trt	21NOV08	1	3.2181	1.5374	72	2.09	0.0399
Date*Trt	21NOV08	2	2.7658	1.5374	72	1.80	0.0762
Date*Trt	21NOV08	3	0	.	.	.	.
Date*Trt	22NOV08	1	1.4029	1.4639	72	0.96	0.3411
Date*Trt	22NOV08	2	0.4524	1.4639	72	0.31	0.7582
Date*Trt	22NOV08	3	0	.	.	.	.
Date*Trt	23NOV08	1	0.8017	1.2478	72	0.64	0.5226
Date*Trt	23NOV08	2	1.0593	1.2478	72	0.85	0.3987
Date*Trt	23NOV08	3	0	.	.	.	.
Date*Trt	24NOV08	1	0	.	.	.	.
Date*Trt	24NOV08	2	0	.	.	.	.
Date*Trt	24NOV08	3	0	.	.	.	.

Type 3 Tests of Fixed Effects

Effect	Num	Den	F Value	Pr > F
	DF	DF		
Date	12	72	60.86	<.0001
Trt	2	72	154.15	<.0001
Date*Trt	24	72	16.51	<.0001

\*\*\*\*\*

autoregressive

The Mixed Procedure

Least Squares Means						
Effect	Trt	Estimate	Standard Error	DF	t Value	Pr >  t
Trt	1	21.2488	0.4911	72	43.27	<.0001
Trt	2	11.6084	0.4911	72	23.64	<.0001
Trt	3	22.8955	0.4911	72	46.62	<.0001

Differences of Least Squares Means									
Effect	Trt	Trt	Estimate	Standard Error	DF	t Value	Pr >  t	Adjustment	Adj P
Trt	1	2	9.6403	0.6945	72	13.88	<.0001	Tukey	<.0001
Trt	1	3	-1.6467	0.6945	72	-2.37	0.0204	Tukey	0.0527
Trt	2	3	-11.2871	0.6945	72	-16.25	<.0001	Tukey	<.0001

Flux based on the volume of the cake:

autoregressive	
The Mixed Procedure	
Model Information	
Data Set	WORK.CHAMBERFLUX
Dependent Variable	Flux
Covariance Structures	Variance Components, Autoregressive
Subject Effect	Bucket
Estimation Method	REML
Residual Variance Method	Profile
Fixed Effects SE Method	Model-Based
Degrees of Freedom Method	Containment

Class Level Information

Class	Levels	Values
Date	13	12NOV2008 13NOV2008 14NOV2008 15NOV2008 16NOV2008 17NOV2008 18NOV2008 19NOV2008 20NOV2008 21NOV2008 22NOV2008 23NOV2008 24NOV2008
Trt	3	1 2 3
Bucket	9	1 2 3 4 5 6 7 8 9

Dimensions

Covariance Parameters	3
Columns in X	56
Columns in Z	9
Subjects	1
Max Obs Per Subject	117

Number of Observations

Number of Observations Read	117
Number of Observations Used	117
Number of Observations Not Used	0

Iteration History

Iteration	Evaluations	-2 Res Log Like	Criterion
0	1	735.20705100	
1	3	710.16630976	0.00000006
2	1	710.16629307	0.00000000

\*\*\*\*\*

autoregressive

The Mixed Procedure

Convergence criteria met.

Covariance Parameter Estimates

Cov Parm	Subject	Estimate
Bucket		78.8797
AR(1)	Bucket	0.4263
Residual		342.83

Fit Statistics

-2 Res Log Likelihood	710.2
AIC (smaller is better)	716.2
AICC (smaller is better)	716.5
BIC (smaller is better)	716.8

Solution for Fixed Effects

Effect	Date	Trt	Estimate	Standard Error	DF	t Value	Pr >  t
Intercept			136.49	11.8562	6	11.51	<.0001
Date	12NOV08		93.7790	15.1177	72	6.20	<.0001
Date	13NOV08		93.2636	15.1173	72	6.17	<.0001
Date	14NOV08		63.8800	15.1165	72	4.23	<.0001
Date	15NOV08		36.2796	15.1145	72	2.40	0.0190
Date	16NOV08		35.1344	15.1097	72	2.33	0.0229
Date	17NOV08		26.8723	15.0986	72	1.78	0.0793
Date	18NOV08		3.3948	15.0725	72	0.23	0.8224

Date	19NOV08		25.2362	15.0112	72	1.68	0.0971
Date	20NOV08		0.2454	14.8662	72	0.02	0.9869
Date	21NOV08		-10.5935	14.5206	72	-0.73	0.4680
Date	22NOV08		-6.0125	13.6754	72	-0.44	0.6615
Date	23NOV08		-9.8164	11.4508	72	-0.86	0.3941
Date	24NOV08		0	.	.	.	.
Trt		1	34.4800	16.7672	72	2.06	0.0434
Trt		2	19.6736	16.7672	72	1.17	0.2445
Trt		3	0	.	.	.	.
Date*Trt	12NOV08	1	196.16	21.3797	72	9.18	<.0001
Date*Trt	12NOV08	2	-84.6677	21.3797	72	-3.96	0.0002
Date*Trt	12NOV08	3	0	.	.	.	.
Date*Trt	13NOV08	1	242.31	21.3791	72	11.33	<.0001
Date*Trt	13NOV08	2	-76.0441	21.3791	72	-3.56	0.0007
Date*Trt	13NOV08	3	0	.	.	.	.
Date*Trt	14NOV08	1	225.11	21.3779	72	10.53	<.0001
Date*Trt	14NOV08	2	-38.1672	21.3779	72	-1.79	0.0784
Date*Trt	14NOV08	3	0	.	.	.	.

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autoregressive

The Mixed Procedure

Solution for Fixed Effects

Effect	Date	Trt	Standard		DF	t Value	Pr >  t
			Estimate	Error			
Date*Trt	15NOV08	1	186.22	21.3751	72	8.71	<.0001
Date*Trt	15NOV08	2	-33.5801	21.3751	72	-1.57	0.1206
Date*Trt	15NOV08	3	0	.	.	.	.
Date*Trt	16NOV08	1	157.92	21.3684	72	7.39	<.0001
Date*Trt	16NOV08	2	-16.3197	21.3684	72	-0.76	0.4475
Date*Trt	16NOV08	3	0	.	.	.	.
Date*Trt	17NOV08	1	118.08	21.3527	72	5.53	<.0001
Date*Trt	17NOV08	2	2.0860	21.3527	72	0.10	0.9224

Date*Trt	17NOV08	3	0	.	.	.	.
Date*Trt	18NOV08	1	82.9891	21.3158	72	3.89	0.0002
Date*Trt	18NOV08	2	6.0943	21.3158	72	0.29	0.7758
Date*Trt	18NOV08	3	0	.	.	.	.
Date*Trt	19NOV08	1	67.0376	21.2290	72	3.16	0.0023
Date*Trt	19NOV08	2	-22.8639	21.2290	72	-1.08	0.2851
Date*Trt	19NOV08	3	0	.	.	.	.
Date*Trt	20NOV08	1	45.0734	21.0240	72	2.14	0.0354
Date*Trt	20NOV08	2	2.8631	21.0240	72	0.14	0.8921
Date*Trt	20NOV08	3	0	.	.	.	.
Date*Trt	21NOV08	1	35.3798	20.5352	72	1.72	0.0892
Date*Trt	21NOV08	2	28.9174	20.5352	72	1.41	0.1634
Date*Trt	21NOV08	3	0	.	.	.	.
Date*Trt	22NOV08	1	14.0292	19.3400	72	0.73	0.4706
Date*Trt	22NOV08	2	0.4499	19.3400	72	0.02	0.9815
Date*Trt	22NOV08	3	0	.	.	.	.
Date*Trt	23NOV08	1	1.6361	16.1939	72	0.10	0.9198
Date*Trt	23NOV08	2	5.3172	16.1939	72	0.33	0.7436
Date*Trt	23NOV08	3	0	.	.	.	.
Date*Trt	24NOV08	1	0	.	.	.	.
Date*Trt	24NOV08	2	0	.	.	.	.
Date*Trt	24NOV08	3	0	.	.	.	.

Type 3 Tests of Fixed Effects

Effect	Num	Den	F Value	Pr > F
	DF	DF		
Date	12	72	42.44	<.0001
Trt	2	72	138.57	<.0001
Date*Trt	24	72	17.34	<.0001

\*\*\*\*\*

autoregressive

The Mixed Procedure

Least Squares Means

Effect	Trt	Standard		DF	t Value	Pr >  t
		Estimate	Error			
Trt	1	303.55	6.8115	72	44.57	<.0001
Trt	2	165.83	6.8115	72	24.35	<.0001
Trt	3	163.54	6.8115	72	24.01	<.0001

Differences of Least Squares Means

Effect	Trt	Trt	Standard		DF	t Value	Pr >  t	Adjustment	Adj P
			Estimate	Error					
Trt	1	2	137.72	9.6329	72	14.30	<.0001	Tukey	<.0001
Trt	1	3	140.01	9.6329	72	14.54	<.0001	Tukey	<.0001
Trt	2	3	2.2955	9.6329	72	0.24	0.8123	Tukey	0.9692

**Ammonia lost based on three treatments:**

SAS code:

```

proc means;
  by trt;
  var lost7 lost13;
run;

proc glm data=lost;
  title "Tukey's HSD_7 d";
  class trt;
  model lost7=trt;
  means trt/ tukey lines;
  lsmeans trt/adjust=tukey tdiff;
run;

```

```

proc glm data=lost;
title "Tukey's HSD_13 d";
class trt;
model lost13=trt;
means trt/ tukey lines;
lsmeans trt/adjust=tukey tdiff;
run;

```

SAS output:

Flux loss based on surface area:

Ammonia lost during first 7 d and 13 d

---

----- trt=1

The MEANS Procedure

Variable	Label	N	Mean	Std Dev	Minimum	Maximum
lost7	lost7	3	193.0723267	4.4977400	188.2331070	197.1247652
lost13	lost13	3	276.2340686	5.3207921	270.1064517	279.6852551

---

----- trt=2

Variable	Label	N	Mean	Std Dev	Minimum	Maximum
lost7	lost7	3	84.3596879	16.3980297	69.0335738	101.6522854
lost13	lost13	3	150.9096958	16.9177411	135.0510442	168.7176521

---

----- trt=3

Variable	Label	N	Mean	Std Dev	Minimum	Maximum
----------	-------	---	------	---------	---------	---------

```

lost7      lost7      3      183.1230375      5.2601041      177.0498196      186.2352324
lost13     lost13     3      297.6415032      6.2707036      290.4287696      301.7993040

```

\*\*\*\*\*

Tukey's HSD\_7 d

The GLM Procedure

Class Level Information

Class	Levels	Values
trt	3	1 2 3

Number of Observations Read           9  
Number of Observations Used           9

\*\*\*\*\*

Tukey's HSD\_7 d

The GLM Procedure

Dependent Variable: lost7   lost7

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	21671.62543	10835.81272	102.61	<.0001
Error	6	633.58748	105.59791		
Corrected Total	8	22305.21291			

R-Square      Coeff Var      Root MSE      lost7 Mean  
 0.971595      6.693717      10.27608      153.5184

Source	DF	Type I SS	Mean Square	F Value	Pr > F
trt	2	21671.62543	10835.81272	102.61	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
trt	2	21671.62543	10835.81272	102.61	<.0001

\*\*\*\*\*

Tukey's HSD\_7 d                      04:23 Monday, May 4, 2009 77

The GLM Procedure

Tukey's Studentized Range (HSD) Test for lost7

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha                                      0.05  
 Error Degrees of Freedom              6  
 Error Mean Square                      105.5979  
 Critical Value of Studentized Range   4.33902  
 Minimum Significant Difference        25.743

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	trt
----------------	------	---	-----

```

A      193.072    3    1
A
A      183.123    3    3

B      84.360     3    2

```

\*\*\*\*\*

Tukey's HSD\_7 d

The GLM Procedure  
Least Squares Means  
Adjustment for Multiple Comparisons: Tukey

trt	lost7	LSMEAN	
		LSMEAN	Number
1	193.072327		1
2	84.359688		2
3	183.123038		3

Least Squares Means for Effect trt  
t for H0: LSMean(i)=LSMean(j) / Pr > |t|

Dependent Variable: lost7

i/j	1	2	3
1		12.95681 <.0001	1.185796 0.5028
2	-12.9568 <.0001		-11.771 <.0001
3	-1.1858 0.5028	11.77101 <.0001	

\*\*\*\*\*

Tukey's HSD\_13 d

The GLM Procedure

Class Level Information

Class	Levels	Values
trt	3	1 2 3

Number of Observations Read 9

Number of Observations Used 9

\*\*\*\*\*

Tukey's HSD\_13 d

The GLM Procedure

Dependent Variable: lost13 lost13

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	37694.70000	18847.35000	159.79	<.0001
Error	6	707.68503	117.94751		
Corrected Total	8	38402.38503			

R-Square	Coeff Var	Root MSE	lost13 Mean
0.981572	4.495275	10.86036	241.5951

Source	DF	Type I SS	Mean Square	F Value	Pr > F
trt	2	37694.70000	18847.35000	159.79	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
trt	2	37694.70000	18847.35000	159.79	<.0001

\*\*\*\*\*

Tukey's HSD\_13 d

The GLM Procedure

Tukey's Studentized Range (HSD) Test for lost13

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	6
Error Mean Square	117.9475
Critical Value of Studentized Range	4.33902
Minimum Significant Difference	27.207

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	trt
A	297.642	3	3
A			
A	276.234	3	1
B	150.910	3	2

\*\*\*\*\*

Tukey's HSD\_13 d

The GLM Procedure

Least Squares Means

Adjustment for Multiple Comparisons: Tukey

trt	lost13 LSMEAN	LSMEAN Number
1	276.234069	1
2	150.909696	2
3	297.641503	3

Least Squares Means for Effect trt

t for H0: LSmean(i)=LSmean(j) / Pr > |t|

Dependent Variable: lost13

i/j	1	2	3
1		14.13308 <.0001	-2.41416 0.1139
2	-14.1331 <.0001		-16.5472 <.0001
3	2.414159 0.1139	16.54724 <.0001	

Flux loss based on volume:

Ammonia lost during first 7 d and 13 d

----- trt=1 -----

The MEANS Procedure

Variable	Label	N	Mean	Std Dev	Minimum	Maximum
lost7	lost7	3	2758.18	64.2534286	2689.04	2816.07
lost13	lost13	3	3946.20	76.0113153	3858.66	3995.50

----- trt=2 -----

Variable	Label	N	Mean	Std Dev	Minimum	Maximum
lost7	lost7	3	1205.14	234.2575678	986.1939112	1452.18
lost13	lost13	3	2155.85	241.6820161	1929.30	2410.25

----- trt=3 -----

Variable	Label	N	Mean	Std Dev	Minimum	Maximum
lost7	lost7	3	1308.02	37.5721720	1264.64	1330.25
lost13	lost13	3	2126.01	44.7907402	2074.49	2155.71

\*\*\*\*\*

Tukey's HSD\_7 d

The GLM Procedure

Class Level Information

Class	Levels	Values
trt	3	1 2 3

Number of Observations Read 9

Number of Observations Used 9

\*\*\*\*\*

Tukey's HSD\_7 d

The GLM Procedure

Dependent Variable: lost7 lost7

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	4525458.844	2262729.422	112.36	<.0001
Error	6	120833.559	20138.926		
Corrected Total	8	4646292.403			

R-Square	Coeff Var	Root MSE	lost7 Mean
0.973994	8.076416	141.9117	1757.112

Source	DF	Type I SS	Mean Square	F Value	Pr > F
trt	2	4525458.844	2262729.422	112.36	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
trt	2	4525458.844	2262729.422	112.36	<.0001

\*\*\*\*\*

Tukey's HSD\_7 d

The GLM Procedure

Tukey's Studentized Range (HSD) Test for lost7

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	6
Error Mean Square	20138.93
Critical Value of Studentized Range	4.33902
Minimum Significant Difference	355.51

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	trt
A	2758.2	3	1
B	1308.0	3	3
B	1205.1	3	2

\*\*\*\*\*

Tukey's HSD\_7 d

The GLM Procedure

Least Squares Means

Adjustment for Multiple Comparisons: Tukey

trt	lost7 LSMEAN	LSMEAN Number
1	2758.17610	1

2	1205.13840	2
3	1308.02170	3

Least Squares Means for Effect trt  
t for H0: LSMean(i)=LSMean(j) / Pr > |t|

Dependent Variable: lost7

i/j	1	2	3
1		13.40323 <.0001	12.51531 <.0001
2	-13.4032 <.0001		-0.88792 0.6668
3	-12.5153 <.0001	0.887917 0.6668	

\*\*\*\*\*

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The GLM Procedure

Dependent Variable: lost13    lost13

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	6519329.689	3259664.845	147.73	<.0001
Error	6	132388.255	22064.709		
Corrected Total	8	6651717.944			

R-Square	Coeff Var	Root MSE	lost13 Mean
----------	-----------	----------	-------------

0.980097 5.415925 148.5419 2742.688

Source	DF	Type I SS	Mean Square	F Value	Pr > F
trt	2	6519329.689	3259664.845	147.73	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
trt	2	6519329.689	3259664.845	147.73	<.0001

Tukey's HSD\_13 d

The GLM Procedure

Class Level Information

Class	Levels	Values
trt	3	1 2 3

Number of Observations Read 9

Number of Observations Used 9

\*\*\*\*\*

Tukey's HSD\_13 d

The GLM Procedure

Dependent Variable: lost13 lost13

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
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Model	2	6519329.689	3259664.845	147.73	<.0001
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Error	6	132388.255	22064.709		
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Corrected Total	8	6651717.944			
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R-Square	Coeff Var	Root MSE	lost13 Mean
0.980097	5.415925	148.5419	2742.688

Source	DF	Type I SS	Mean Square	F Value	Pr > F
trt	2	6519329.689	3259664.845	147.73	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
trt	2	6519329.689	3259664.845	147.73	<.0001

\*\*\*\*\*

Tukey's HSD\_13 d

The GLM Procedure

Tukey's Studentized Range (HSD) Test for lost13

NOTE: This test controls the Type I experimentwise error rate, but it generally has a higher Type II error rate than REGWQ.

Alpha	0.05
Error Degrees of Freedom	6
Error Mean Square	22064.71
Critical Value of Studentized Range	4.33902
Minimum Significant Difference	372.12

Means with the same letter are not significantly different.

Tukey Grouping	Mean	N	trt
A	3946.2	3	1
B	2155.9	3	2
B	2126.0	3	3

\*\*\*\*\*

Tukey's HSD\_13 d

The GLM Procedure

Least Squares Means

Adjustment for Multiple Comparisons: Tukey

trt	lost13 LSMEAN	LSMEAN Number
1	3946.20098	1
2	2155.85280	2
3	2126.01074	3

Least Squares Means for Effect trt

t for H0: LSMean(i)=LSMean(j) / Pr > |t|

Dependent Variable: lost13

i/j	1	2	3
1		14.76162	15.00767
		<.0001	<.0001

2	-14.7616		0.246051
	<.0001		0.9674
3	-15.0077	-0.24605	
	<.0001	0.9674	