ABSTRACT

Analysis of Ammonia and Volatile Organic Amine Emissions in a Confined Poultry Facility

by

Hanh Hong Thi Dinh, Master of Science

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Major Professor: Dr Robert S. Brown

Department: Chemistry and Biochemistry

The National Air Emission Monitoring Study (NAEMS) project was funded by the Agricultural Air Research Council (AARC) to evaluate agricultural emissions nationwide. Utah State University (USU) is conducting a parallel study on agricultural emissions at a Cache Valley poultry facility. As part of this parallel study, samples of animal feed, eggs and animal waste were collected weekly from three manure barns (designated: manure barn, barn 4 - manure belt and barn 5 - high rise) from May 2008 to November 2009.

These samples were analyzed to determine ammonia content, total Kjeldahl nitrogen content and ammonia emission. The yearly average calculated NH_3 values for manure barn, barn 4 and barn 5 were determined in units of mg NH_3/g_{manure} as: 1.1 ± 0.2, 0.6 ± 0.1 and 0.8 ± 0.1, respectively. The yearly average calculated TKN values in units

of % N were determined as: 2.0% ± 0.3, 1.6% ± 0.3 and 1.9% ± 0.3 for manure barn, barn 4 and barn 5, respectively. The yearly average of NH_3 emission in units of mg NH_3/bird-day was determined to be 440 ± 180 mg NH_3/bird-day for barn 4, and 540 ± 190 mg NH_3/bird-day for barn 5.

The ammonia and organic amines emissions in ambient air at a Cache valley confined poultry facility were measured by using a sulfuric acid trapping solution in an impinger train followed ion chromatography (IC) detection. The yearly average concentrations of ammonia in ambient air at the barns were calculated at 11.9 ± 2.9 ppm at the manure belt barn and 12.7 ± 3.1 ppm at the high rise barn. No organic amines were detected in the collected ambient air samples by the ion chromatography method.

Because there were no amines detected by the IC method, limits of detection of organic amines in air were studied. The results showed that the organic amines in the manure must occur at a minimum concentration of 1 ppm in order to have sufficient vapor pressure so that enough is transported to the impingers for trapping and subsequently be detected by the IC.

(104 pages)

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CHAPTER 1

INTRODUCTION

Introduction

Animal agriculture in the United States accounts for a significant segment of the U.S agriculture. It includes beef, dairy, goats, poultry, sheep, and swine. Livestock and livestock products generated from $87.1 billion to $96.5 billion annually which represents 46 to 48 percent of U.S. cash receipts from farm marketing between 1995 and 1998 (National Research Council, 2003). Meat, dairy products and eggs are important components of the U.S. diet and livestock agriculture provides the basis for these needs. The U.S. has the largest feed-cattle industry in the world and is the world's largest producer of beef. Among livestock industries, milk has a farm value of production second only to beef. The U.S. is also the world's third largest producer and second largest consumer, exporter, and importer of pork and pork products. The U.S. poultry industry is the world's largest producer and second largest exporter of poultry meat (Robert, 2007). Livestock and poultry are raised on an estimated 1.3 million farms throughout the nation. About 238,000 of these farms are considered animal feeding operations (AFO), agriculture enterprises where animals are kept and raised in confinement (Claudia, 2006). Concentrated Animal Feeding Operations (CAFOs) are AFOs that meet certain EPA criteria. CAFOs make up approximately 15 percent of total AFOs. In addition to its significant contribution to the nation's economy, livestock agriculture also contributes significantly to the U.S. job market. According to the National Research Council (2003) meat products represent 49.8 percent of all non-metro food processing employment and 1

of 16 rural manufacturing jobs. In many states (Alabama, Colorado, Delaware, New Mexico, New York, Oklahoma, Pennsylvania, Utah, Vermont, West Virginia and Wyoming), livestock agriculture accounts for more than 65 percent of the revenue generated from farming.

Between 1982 and 1997, the number of animal feeding operations in the United States decreased by 51 percent, while livestock production increased by 10 percent. In some areas, even greater changes in concentration have occurred (National Research Council, 2003). Food demand increases as the population grows. During the past few decades, the increasing concentration of food production (meat, eggs, milk, etc.) from animals in very large feeding operations has focused public attention on the associated with environmental issues (National Research Council, 2003). These include the effects of air emissions, especially those that come from the large quantities of manure also produced by the animals. One of the biggest public policy concerns is focused on the impacts of these large operations on available water resources. If animal wastes are not managed properly, they can adversely impact water quality through surface runoff and erosion, direct discharges to surface waters, and leaching into soil and groundwater (Claudia, 2006). Animal feeding operations (AFO) can also affect air quality through emissions of gases and aerosol such as ammonia, hydrogen sulfide, particulate matter (PM), volatile organic compounds (VOCs), hazardous air pollutants, microorganisms, and odor. In addition, AFOs also produce gases such as carbon dioxide and methane that have been associated with climate change (Jeff and Holly, 2009). The generation rates of odor, manure, gases, particulates, and other constituents vary with weather, time, animal species, type of housing, feed type, and different manure management system used for

storage and handling (National Research Council, 2003; Claudia, 2006). Within the livestock facilities, emission sources include barns, feedlot surfaces, and manure storage area, the bulk of air emissions come mostly from the microbial breakdown of manure stored in pits or lagoons and spread on fields. Each emission source will have a different profile of substances emitted, with rates that fluctuate through the day and the year. Pollutants associated with AFOs have a number of environmental and human health impacts, most regulatory concerns are focused on possible health effects.

Ammonia (NH_3) emission

Agriculture activities, in particular livestock production, have been reported to be the largest contributor of NH_3 emissions into the atmosphere. According to the U.S Environmental Protection Agency's emission inventory (USEPA, 2002, 2004), livestock operations and fertilizer application constituted about 85% of the total national NH_3 emissions. Publicly owned treatment works, mobile sources and combustion sources make up the remaining 15%. In both Europe and the United States, the largest source of ammonia emissions is livestock, estimated to account for 70–90% of total emissions, and dairy cows are one of the largest livestock sources (Battye, 1994; USEPA, 2002; Pain et al., 1998; Hutchings et al., 2001). Livestock and poultry diets consist of high-protein feed which contains surplus nitrogen to ensure that the animal's nutritional requirements are met. Nitrogen that is not metabolized into animal protein is excreted in the urine and feces of livestock and poultry where further microbial action releases ammonia into the air during manure decomposition (Susan and Katharine, 2005; Faulkner and Shaw, 2008). Ammonia is a common by-product of microbial decomposition of the organic nitrogen compounds in manure. Nitrogen in the urine is in the form of urea, $(NH_2)_2CO$, which can

rapidly hydrolyze to form ammonium carbonate. As shown in reactions (1), (2) and (3), dissociation of ammonium carbonate produces ammonium ions that can further decompose and be volatilized as gaseous ammonia. Hydrolysis is facilitated by the enzyme urease, which is abundant in soils and plant roots as well as in animal feces.

$$(NH_2)_2CO + 2H_2O \rightleftharpoons (NH_4)_2CO_3 \quad (1)$$

$$(NH_4)_2CO_3 + H_2O \rightleftharpoons 2NH_4^+ + HCO_3^- + OH^- \quad (2)$$

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \quad (3)$$

Ammonia (NH_3) is produced within livestock buildings, in open feedlots, in manure storage facilities, during manure handling and treatment and when manure is applied to soils as fertilizer. Ammonia is a colorless, lighter than air gas that has a strong, sharp and pungent odor. Ammonia disperses rapidly in the air (Battye et al., 1994) and can be easily removed from livestock buildings by proper ventilation. As ammonia is highly water soluble, it will be washed out of the air by precipitation and returned to the earth's surface. It can also be deposited as dry salt deposits near the emitting source (Holger et al., 1998). Because ammonia is a very basic compound, it can form salts by reaction with acidic gases in the atmosphere and these can be transported long distances, especially in the absence of clouds. Ammonia in the atmosphere reacts with acidic compounds such as nitric acid or sulfuric acid to form fine particulate matter $PM_{2.5}$ composed primarily of ammonium nitrate and ammonium sulfate. Reactions of ammonia with sulfuric acid and nitric acid were shown in equations (4), (5) and (6).

$$NH_3(g) + H_2SO_4(g,l) \rightarrow NH_4HSO_4(s,l) \quad (4)$$

$$NH_3(g) + NH_4HSO_4(l) \rightarrow (NH_4)_2SO_4(s, l) \quad (5)$$

$$NH_3(g) + HNO_3(g) \rightarrow NH_4NO_3(s) \quad (6)$$

It can be seen that the control of ammonium-based PM may ultimately be based on NH_3 controls. Ammonium sulfate is preferential under most conditions, though ammonium nitrate favored by low temperature and high relative humidity. The Cache valley is unique in its air quality problems. Despite a small amount of heavy industry there are significant levels of $PM_{2.5}$ during the wintertime. One of the pollutants that seems particularly specific to the Cache valley is ammonium nitrate. Ammonium nitrate is a particle that is formed through complex chemical reactions in the air. The reactions involve ammonia and nitrogen oxide gases that combine to form a particle. The rate at which particles form and the particles life span is increased when the weather is very cold and foggy, conditions that often occur under Cache valley's wintertime inversions. Emission inventory of ammonia contain uncertainties. Researchers are seeking improvements through process-based inventory approaches for AFOs. Monitoring of ammonia gas is important for identifying $PM_{2.5}$ formation. However, there are limited numbers of such monitoring sites.

On a global scale, animal farming systems emit to the atmosphere ~20 Tg N/yr as NH_3. This is about 65 percent of the total NH_3 emitted by terrestrial sources (National Research Council, 2003). Teragram (Tg) is a metric unit of mass equal to 10^{12} grams or 1 megatonne (one million metric tons). This unit is frequently used in atmospheric science and other scientific contexts where large masses are considered. In the United States, about 6 Tg N/yr is consumed by animals in feed, of which about 2 Tg N/yr is emitted to the atmosphere as NH_3 and about 1 Tg N/yr is consumed by humans in meat products (National Research Council, 2003). A recent ammonia emission inventory of UK agriculture estimated emission levels as 197 kt NH_3-N $year^{-1}$ (Misselbrook et al., 2000;

Pain et al., 1998). Kt is an abbreviation of kiloton (kt), a unit of mass equal to 1,000 metric tons.

Ammonia is typically considered an indoor air quality concern by livestock and poultry producers because the gas often accumulates inside poorly ventilated or poorly managed animal facilities (Susan and Katharine, 2005). High NH_3 concentrations in animal housing units may cause decreased production rates and chronic health problems in both animals and human workers (Yang et al., 2000). Ammonia can also have a negative impact on human health. At moderate levels of concentration, ammonia can irritate the eyes and respiratory tract. At high concentrations, it can cause ulceration to the eyes and severe irritation to the respiratory tract. Exposure to even low levels of ammonia can irritate the lungs and eyes. Table 1 lists the health effects of ammonia with different doses of exposure.

Table 1. Health effects of ammonia (Atta, 2006).

Concentration (ppm)	Health response
20-50	Nose and throat irritation after ten minutes of exposure
72-134	Irritation of nose and throat after five minutes of exposure
700	Immediately and severe irritation of respiratory system
5000	Respiratory spasms, rapid suffocation
Above 10,000	Pulmonary edema, potentially fatal accumulation fluid in lungs and death

Gas emission rates are often normalized to the number and weight of animals by dividing the total emission rate by the number of animal units (AU), where one AU is equal to 500 kg of animal live weight. Emission expressed in terms of AU is often

referred to as the emission factor. Various attempts of measurement ammonia concentration have been made to quantify NH_3 emission from livestock production facilities (Groot et al., 1998; Hinz and Linke, 1998; Burns et al., 2003). However, currently there are limited data in ammonia emission rates from U.S. commercial layer houses. Even though ammonia emissions from various European production facilities have been quantified (Groot et al., 1998; Hinz and Linke, 1998), it may not be readily applicable to US counterparts, due to the differences in housing facilities, manure management practices, climate, etc.

A recent ammonia emission inventory from UK agriculture estimated emission as 197 kt NH_3-N $year^{-1}$ (Pain et al., 1998). Emissions from poultry housing accounted for 12% of this value. Table 2 lists published ammonia emissions from poultry housing.

Table 2. Ammonia emission factors from poultry housing.

Production unit	Notes	Emission Factor g NH_3 AU^{-1} day^{-1}	References
Layer	Deep litter	177-261	Groot et al. 1998
Broiler	Litter	53-200	Groot et al. 1998
Broiler	Litter	5.8-8.4	Zhu et al. 2000
Layer	Summer	300	Wathes et al. 1997
Layer	Manure belt	14-224	Groot et al. 1998
Layer	Winter	190	Wathes et al. 1997

Airborne Particulates

Airborne particles are highly complex in size, physical properties and composition. For regulatory purpose, airborne particulate matter (PM) is commonly

considered as either coarse particles, those less than 10 microns in diameter and referred to as PM_{10} or fine particles, those less than 2.5 μm in diameter and referred to as $PM_{2.5}$. Agriculture is a major source of PM_{10} due to dust generated from storage facilities, feeding equipment, and in other mechanical processes (Claudia, 2006). In contrast, fine particulate matter, $PM_{2.5}$, results from evaporation combined with atmospheric chemical processes and also by direct emission. Fine particles are formed in the atmosphere through the reactions of gases such as sulfur oxide, nitrogen oxide and VOCs and NH_3.

Animal feeding operations can contribute to particulate matter through several mechanisms, including animal activities and animal housing ventilation units. Particulate matter can contribute indirectly to fine particles formation by emission of ammonia which is subsequently converted to aerosols through reactions in the atmosphere. Particle formation is highly dependent on atmospheric temperature, humidity and concentrations of the precursors compounds, so particle formation is variable and difficult to predict. However, particles of different sizes can have significantly different health effects. Larger particles tend to be deposited in the upper airways of the respiratory tract, whereas small particles (e.g., $PM_{2.5}$) can be inhaled deeper into the lungs, and can cause a variety of respiratory and cardiovascular aliments (Shabtai and Robert, 2009). The secondary effect of airborne particles is related to haze and decrease in visibility, due to aerosols that both absorb and scatter light. The airborne $PM_{2.5}$ particulate matter plays a major role in formation of regional haze and associated with low visibility. In the United States, haze has reduced natural visibility from 90 miles to between 15 and 25 miles in the East and from 140 miles to between 35 and 90 miles in the West (EPA, 2002, 2004). Visibility

in the eastern United States is generally worse than in the west, due to higher average humidity levels and higher levels of particulate matter (Susan and Katharine, 2005).

Hydrogen sulfide (H_2S) emissions

Hydrogen sulfide (H_2S) is a colorless gas with a strong and generally objectionable rotten egg odor. It is produced in anaerobic (oxygen-deprived) environments from microbial reduction of sulfate in water and the decomposition of sulfur-containing organic matter in manure. Acute human health effects include respiratory and cardiovascular irritation, as well as headaches (Claudia, 2006). Within agriculture activities, the major concern relating to hydrogen sulfide emission relates to complaint about its odor.

Methane and Nitrous Oxide emission

Methane (CH_4) and Nitrous Oxide are classified as greenhouse gases known to contribute to climate change. Total global anthropogenic CH_4 is estimated to be 320 Tg CH_4/yr (National Research Council, 2003), comparable to the total from natural sources. Of the various anthropogenic sources, the agricultural sector is the largest, with livestock production being a major component within this sector. In the United States, livestock emissions contribute 7.6 Tg CH_4/yr of a total anthropogenic source of 41 Tg Ch_4/yr (National Research Council, 2003). EPA estimates that 25 percent of the nation's methane emissions come from livestock (Shih et al., 2006). Agriculture methane is produced by ruminant animals, but also is emitted during microbial degradation of organic matter under anaerobic conditions (Claudia, 2006). The most important factor affecting the amount of methane produced is how the manure is managed, because some types of storage and treatment systems promote an oxygen-depleted (anaerobic)

environment. Metabolic processes of methanogens lead to CH_4 production at all stages of manure handling. Higher temperatures and moist conditions also promote CH_4 production (National Research Council, 2003). Sommer and Moller (2000) estimated that methane may contribute between 9 and 20% of the total gaseous global warming potential.

Nitrous oxide forms and is emitted to the atmosphere via the microbial processes of nitrification and denitrification. Nitrification is the biological oxidation of ammonia with oxygen and is sequentially oxidized to nitrite and nitrate. Denitrification is the opposite process where the reduction takes place to reduce nitrite or nitrate into molecular nitrogen. Global emissions in 1990 were about 15 Tg N/yr, of which anthropogenic sources accounted for ~3 Tg N/yr (National Research Council, 2003). Of these, N_2O emissions from animal excreta accounted for about 1 Tg N/yr. In the United States, total anthropogenic sources in 1990 were about 0.4 Tg N/yr, with animal excreta contributing about 25 percent (National Research Council, 2003).

Ammonia Odor

Odor generated from agriculture activities is becoming one of the biggest agricultural related public complaints, mainly from neighborhoods near AFOs (National Research Council, 2003). Livestock and poultry odors originate from four primary sources: animal buildings, feedlot surfaces, manure storage units, and land application of manure. Of these four sources, land application of manure is probably the biggest source of odor emissions and complaints. Odor from AFOs is not caused by a single substance, but is the result of a large number of contributing compounds, including ammonia, VOCs, and hydrogen sulfide. Volatile organic compounds include a large number of

constituent classes such as volatile fatty acids, organic sulfides, amines, alcohols, hydrocarbons and halocarbons. In terms of their health and environmental effects, some VOCs may irritate skin, eyes, nose and throat (Susan and Katharine, 2005). Information on VOC emissions from animal housing is limited. Zahn et al. (2001) measured VOC emissions from swine houses during August and September of 1997. Twelve different non-methane VOCs were detected at a total concentration of 806 $\mu g\ m^{-3}$. The VOC mixture consisted primarily of acetic, propionic and butyric acid.

In order to understand the potential health and environmental impacts of AFOs, estimates of air emissions at the individual farm level are needed. Their dependence on management practices are also needed to characterize annual emission inventories for these pollutants. Some problems caused by animal feeding operations have occurred, in part, due to the concentration of production in large operations, which is driven by market economics. High production in agricultural regions requires producers to modify their existing practices to reduce harmful emissions. At this time, the majority of data for emissions from animal feeding operations are from Europe where buildings, manure management, and climate are often different than in the U.S. Previously, little research on ammonia emissions has occurred in the U.S., although research is increasing (Arogo et al., 2003).

National Air Emission Monitoring Study (NAEMS)

Due to the fact that many AFOs have increased in size, AFO emissions have been brought under federal regulations. These regulations include the 1990 Clean Air Act (CAA), the 1980 Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), and the 1986 Emergency Planning and Community Right-to-Know Act

(EPCRA). However, the currently available scientific data related to livestock air emissions which are needed to properly regulate AFOs under the CAA, CERCLA, and EPCRA are limited. Prompted by legislation, especially the Clean Air Act (CAA), and by public concerns, the U.S. Environmental Protection Agency (EPA) has been considering what information is needed to define and support feasible regulation of air emissions from AFOs. In order to address the lack of scientific data, the National Air Emission Monitoring Study (NAEMS) was established in 2006 by a voluntary Air Compliance Agreement between the EPA and the pork, dairy, egg and broiler industries. Livestock producers have provided the financial support for the NAEMS so that emissions data can be collected at select sites. The objectives of the NAEMS study are to accurately assess emissions from livestock operations and compile a database for estimation of emission rates, and therefore to promote a national consensus for emissions-estimation methods/procedures from livestock operations.

The National Air Emission Monitoring Study (NAEMS) project has been funded by the Agricultural Air Research Council (AARC) to evaluate agricultural emissions nationwide beginning in 2006. The NAEMS is overseen by the EPA Office of Air Quality Planning and Standards (OAQPS) and the project is managed by Purdue University. The project is designed to develop methods to quantify air emissions from the U.S. confined animal feeding operations and to perform air monitoring at various poultry, dairy and swine operations to measure emissions from these operations. Results from these studies are aimed at evaluating different management practices to determine if they are affective at reducing NH_3 air emissions. Utah State University (USU) is conducting a parallel study on agricultural emissions at a Cache Valley poultry farm. A parallel effort

has been run with separate funding at USU to help validate the methods developed by the Purdue University researchers as part of NAEMS. Experiments were carried out to determine the ammonia and amines gas emissions in ambient air at a local livestock facility. Measurements were conducted to determine the total Kjeldahl nitrogen (TKN) and the nitrogen loss to the atmosphere of the animal production and waste. Animal production includes feed and eggs. Animal waste includes its manure.

Amines Emission

Amine emissions have been studied by various researchers to establish their inherent toxicity and the potential carcinogenicity of their reaction products (Akyuz, 2007). Aliphatic amines such as methylamine, dimethylamine, ethylamine, diethylamine, etc., are known to be important in air pollutants due to their odorous and toxic characteristics (Akyuz, 2007). It is well known that they can react with nitrite, nitrate, NOx or OH radicals in the environment and can form toxic carcinogenic N-nitrosamines (Skarping and Bellander, 1986; Santagati et al., 2002). Additionally, most alkylamines are irritants to the skin, mucous membrane and respiratory tract. Monitoring of the levels of aliphatic amines in ambient air is important to prevent human exposure to these compounds through inhalation, and minimize any health associated problems.

Currently, environmental concentrations of aliphatic amines are poorly known. To date, only a few studies of atmospheric aliphatic amines have been reported, mostly in the geographic of strong sources of emission. Michael et al. (2007) measured concentration of amines in air using test chamber method. Sampling of test chamber air was done by drawing 50 L of air through sampling tubes. Quantification of sampled analytes was achieved by Liquid Chromatography and Mass Spectrometry (LCMS) analysis. The

concentration of triethylamine and trimethylamine in air was reported as 16.5 μg/m^3 and 1.2 μg/m^3, respectively. In another study, Schiffman et al. (2001) analyzed the volatile organic compounds (VOCs) in air and lagoon water at swine operations in North Carolina. VOCs from air were collected onto cartridges packed with Tenax and analyzed by gas chromatography mass spectrometry (GC/MS). The results from the samples contained some of amine compounds including methylamine, ethylamine and trimethylamine and their concentrations were reported as 0.0186 mg/m^3, 0.324 mg/m^3 and 0.0024 mg/m^3 respectively. Table 3 shows a summary of previous studies of amines in animal agriculture.

The most widely used techniques for the determination of aliphatic amines in air samples are gas chromatography (GC) coupled with a variety of detectors (Akyuz, 2007; Zhu and Aikawa, 2004; Namiesnik et al., 2003). The trace determination of low-molecular-mass aliphatic amines in air has been performed by GC with nitrogen selective detectors such as nitrogen-phosphorus thermionic detection (NPD), chemiluminescent detection (CLD), and gas chromatography mass spectrometry (GC-MS) using either direct injection or the headspace analysis technique. Derivatization methods have also been used in water and soil samples, because these samples cannot be directly analyzed without further sample preparations (Kataoka, 1996). Kataoka (1996) reported the determination of trace amounts of twelve aliphatic primary and secondary amines as their derivatives in waters from sewage and rivers by a GC-MS method.

This group found low molecular mass aliphatic amines in water samples can be determined down to detection limit of 1-3 ppb. Kataoka (1996) reported that secondary amines as their derivatives (N-dimethylaminomethylene) had been determined in

cigarette smoke using gas chromatography coupled with flame photometric detection (GC-FPD).

Table 3. Amines studies in animal agriculture.

Compound	Facility type	Concentrations in air ppb	References
Methylamine	swine	18	Schiffman et al. 2001
Methylamine	swine	24	Devos et al. 1990
Ethylamine	swine	324	Schiffman et al. 2001
Ethylamine	swine	603	Devos et al. 1990
Trimethylamine	swine	2.4	Schiffman et al. 2001
Triethylamine	swine	309	Schiffman et al. 2001
Tributylamine	dairy	5.25	Filipy et al. 2006
Trimethylamine	dairy	2.4	Filipy et al. 2006

This method is selective and sensitive to secondary amines, and the detection limits of the amines are 0.05-0.2 pmol. By using this method, it was confirmed that dimethylamine, pyrrolidine, piperidine and morpholine occur in the main and the side stream of smokes from cigarettes and the contents of these amines in side stream smoke are very high compared with those in main stream smoke (Kataoka, 1996).

Amines in general are difficult to analyze by GC due to their interaction with the GC column often leads to significant tailing and poor reproducibility (Sze and Borke, 1962). For this reason, derivatization methods have typically been employed to reduce the polarity of the amino group and to improve the detection and separation of amines. Derivatization methods are time-consuming and there are some potential problems with

derivatization procedures, including the formation of unwanted derivatives, the presence of unreacted derivatization reagents and a requirement for non-aqueous reaction conditions (Kataoka, 1996).

To overcome the difficulties associated with GC methods, ion chromatography (IC) techniques have been employed for the determination of low molecular mass organic ionic species such as C1-C5 carboxylic acids, sulfonic acids and amines (Yan et al.2002). These species are separated based upon differences in their electrostatic features, such as the degree of charge, rather than hydrophobicity or polarity as in reversed phase LC.

Yan et al. (2002) determined the aromatic amines in waste water samples by using Cation Exchange Chromatography method. This group reported the concentrations of benzidine, *p*-Chloroaniline, and 1-Naphthylamine in wastewater samples were 0.146 µg/ml, 0.129 µ/ml and 0.679 µ/ml, respectively. In another application, Cinquina et al. (2004) had determined some biogenic amines in tuna fish by ion exchange chromatography with conductivity detection. The limits of detection (LODs) were reported as 0.15 mg/kg for cadaverine, 0.15 mg/kg for putrescine and 0.45 mg/kg for histamine. Brian et al. (2007) determined biogenic amines in alcoholic beverages by using ion chromatography with suppressed conductivity detection and integrated pulsed amperometric detection (IPAD). IPAD detects more biogenic amines than suppressed conductivity detection, thus enable the detection of dopamine, tyramine, and serotonin in beverages. This group found the sensitivity for the ten biogenic amines varied considerably from 0.004–1.1 mg/l and recoveries were within 85–122% (Brian et al., 2007).

Although IC has been successfully applied to the analysis of amines in various samples, no studies have been reported in the literature for using IC to analyze organic amines in AFOs.

Ion Chromatography

Ion chromatography is a form of liquid chromatography that uses the principle of ion-exchange resins to separate and quantify organic and inorganic ions based on their interaction with the resin (Brian, 2007). The technique was introduced in 1975 by Small, Stevens, and Baumann and has developed into a mature analytical technique for the separation and determination of both organic and inorganic cations and anions (Weiss, 1995). One of the major applications of IC is for the analysis of anions for which there are no other rapid analytical methods (Paul et al., 2003). It is also commonly used for cations and biochemical species such as amino acids and proteins. Ion chromatography is also a widely used technique in the semiconductor industry. This is because it can provide quantitative analysis of anions in the ppb range, making it capable of detecting contaminants on the surface of a wafer, die, or package (James and Douglas, 2000).

Ion chromatography incorporates a mobile phase and stationary phase. The mobile phase in this case is usually water and some pH buffer mixture. A tubular column that contains an ion exchange resin serves as the stationary phase for the separation. The sample is passed through the column by a constant flow of the mobile phase. Analytes (cations or anions depending on the resin employed) selectively interact with the stationary phase resulting in a differential mitigation of the various analytes. Since each ion has a different affinity for the stationary phase resin, some ions will spend less time while others will spend more time in the mobile phase. The fact that each ion has a

different residence time in the stationary phase allows for their temporal separation. Eventually, each ion elutes from the column and ionic species are detected by a conductivity detector. The resulting ion chromatogram can be quantified by the area under each ion peak which represents the relative amount of each ion in a sample.

In this thesis, IC provides a convenient method for separating, identifying and quantifying amines collected from atmospheric samples. Organic amines are separated based on their relative affinity for a cation-exchange resin. They are also separated from ammonia and alkali cations, and subsequently quantified based on their conductivity. Ammonia and amines in ambient air were sampled through an impinger train and analyzed with IC utilizing an electrochemical suppressor prior to the conductivity detector (Morris, 1977). The impinger sampling train method is discussed in detail in chapter 2 of this thesis. To our knowledge, there have not been any other prior studies on amine emissions characterized using IC reported in the literature. The analysis of ammonia and organic amine emissions in ambient air at a local livestock facility using ion chromatography detector is discussed in detail in Chapter 2.

Total Kjeldahl Nitrogen (TKN)

The Kjeldahl method was developed over 100 years ago by Johan Kjeldahl for the determination of nitrogen content in organic and inorganic substances. Total Kjeldahl nitrogen or "TKN" is defined as the total organic nitrogen and ammonia nitrogen in a sample. The level of organic nitrogen is then determined by subtraction after first determining the ammonia component. This method basically converts organic nitrogen to ammonia and then tests for total ammonia. The Kjeldahl method is broken down into

three main steps: digestion, distillation, and titration. Chemical reactions of TKN analysis were discussed in detail in Chapter 3 of this thesis.

Total Kjeldahl nitrogen is a wet oxidation procedure used to determine the NH_3 present in soils, plants, and organic residues such as dairy manure. Also, TKN analysis can include a pretreatment of the sample to convert nitrate nitrogen NO_3-N and nitrite nitrogen NO_2-N to NH_3, which then provides a total N analysis.

Manure composition can significantly affect its emissions, both in terms of general odor and individual chemical components. The total nitrogen content is an important manure property that effects emission of ammonia and other nitrogen containing compounds. According to a manure analysis program conducted by the University of Maryland, the average total N content was 2.4% for 400 samples of dairy manure collected from 1985 to 1990 (Brady and Weil, 1996). Zhang and Hamilton (1998) reported values from 1.29% to 1.93% N for feedlot manure. Iversen et al. (1997) reported values of 1.2% N in samples of composted dairy manure.

In the studies reported in Chapter 3 of this thesis, the TKN of animal waste and production from a poultry farm is determined by using the “macro Kjeldahl” method. Organic nitrogen in a manure sample was first converted to ammonia by metal catalyzed acid digestion. The ammonia in the digest sample is then distilled away from the rest of the sample. The ammonia concentration of the distillate is then determined by titration with sulfuric acid. Chapter 3 deals with determining the ammonia content of manure samples and determining the total nitrogen content of manure, feed and egg samples.

Nitrogen Balance Calculations

Ammonia nitrogen (NH_3-N) in livestock manure represents one of the most important sources of manure N losses to the atmosphere (Yang et al., 2000). Excess nitrogen loss from animal waste can indicate inefficiencies in protein utilization, decreased manure fertilizing value and reduced profitability. The N content of manure varies greatly from farm to farm depending on animal diet, amount of bedding added, water added from rain or milk house waste, etc. (Jokela and Meisinger, 2004). Most of the nitrogen lost from animal production systems is volatilized ammonia, and it can be used to quantify nitrogen emissions. Emission rates are usually expressed in terms of mass of NH_3 or ammonia nitrogen (NH_3-N) per unit time and per animal (or live weight units) or per unit area (surface sources).

Measurements of individual emissions (e.g., ammonia volatilization, N runoff, and nitrate leaching) are difficult and expensive, leading to the predicament that few data are available on which to base mathematical models for predicting individual emissions (National Research Council, 2003). Mass balance-based method calculates emission or Nitrogen loss to the environment by the difference between all inputs (N_{input}) and measurable outputs (N_{output}) the system under study. Using this technique, NH_3 emissions could be estimated by performing a mass balance for nitrogen. A mass balance for N establishes an upper limit for the estimation of NH_3 emissions after adjusting the N loss by a factor of 17/14 to account for the difference in molecular weight between N and NH_3.

$$N_{loss} = N_{input} - N_{output}$$

In Chapter 3, nitrogen concentration of all materials, including animal flesh and production such as milk and eggs for dairy and egg layers entering and leaving the monitored housing facility will be determined or estimated using a nitrogen balance calculation method. Feed, fresh bedding, manure, milk and eggs will be chemically analyzed for total nitrogen. Data on feed consumption quantities and amount of bedding used will be obtained from the producers.

Chapter 2 of this thesis focuses on the results of a study that measured the levels of ammonia and organic amines emitted from a local poultry farm (an AFO) using ion chromatography detection. The total nitrogen content of animal products and waste as well as their ammonia content will be determined using total Kjeldahl titration method. A total nitrogen balance (in-take vs. out-take) will be calculated.

CHAPTER 2

ANALYSIS OF AMMONIA AND VOLATILE ORGANIC AMINE EMISSIONS IN A CONFINED POULTRY FACILITY USING ION CHROMATOGRAPHY

1. Introduction

Agricultural practices are known to input large amounts of nitrogenous species into the atmosphere (Miller and Varel, 2001). During the past few decades, large livestock confinement buildings are becoming more common because they effectively reduce unit costs of production. But they can also be significant sources of aerial pollutants (Lim et al., 2006). As mentioned in the introduction chapter (Chapter 1), ammonia emissions from agriculture are a significant source of atmospheric reactive nitrogen that can lead to negative impacts for both animal and human health. In addition to ammonia, amines emissions from animal livestock facilities are often correlated with those of NH_3 and consist of methylamine, ethylamine, and dimethylamine (Schiffman et al., 2001; Filipy et al., 2006). Thus, identifying and quantifying the amounts of ammonia and amine emissions in animal feeding operations are needed.

In this study, a method for identifying and quantifying ammonia and volatile organic amine emissions in ambient air at a local facility in Catch Valley has been developed using ion chromatography (IC). Amines were separated based upon differences in affinity toward a cation-exchange resin (which provides separation from ammonia and alkali cations), and quantified based on conductivity measurements. Previous research (Frank et al., 2006; Audunsson et al., 1989) has shown that amines in

livestock air can be more efficiently sampled using sulfuric acid impingers and these can subsequently be analyzed using Ion Chromatography.

2. Experimental section

2.1. Sampling

Impingers are Pyrex glass bubble tubes designed for the collection of airborne hazards into a liquid medium. When used to sample air, a known volume of air is pumped through the glass tube that contains a trapping liquid. In this study, 0.1 N H_2SO_4 solution was used as the trapping solution. A known volume of air was drawn from the barn ambient air through a series of collecting vessels. The sampling train consisted of two midget bubblers and two midget impingers (Part # 737560-0000, Kimble/Kontes, Vineland, NJ). The first two impingers (#1 and #2) each contained 15 mL of 0.1N H_2SO_4 solution. The first bubbler captured most of the amines emitted from the sample source. However, if the acid solution were to become saturated due to high amine concentrations, the second bubbler would retain the surplus amines. The third impinger (#3) was empty to trap any over flow of sulfuric acid from the second bubbler. The fourth impinger (#4) was filled with 15 mL silica gel (6–12 mesh). Sampling ports between impingers were connected with non-outgassing tubing (polyetheretherketone tubing, 10-mm ID; PEEK). The sampling train was assembled in a ring stand for stability and the first two impingers were placed into a beaker of ice to avoid evaporation. Air was pulled through the sampling train at a rate of 1 L min^{-1}. The flow rate was measured with a DC-Lite primary flow meter (Bios, NJ). The DC-Lite primary flow meter was calibrated before taking the measurement. Each sampling period was 2 h, resulting in a total of typically 120 L of air

sampled through the acid solution. Fig. 1 shows a drawing of the impinger sampling train employed for these studies.

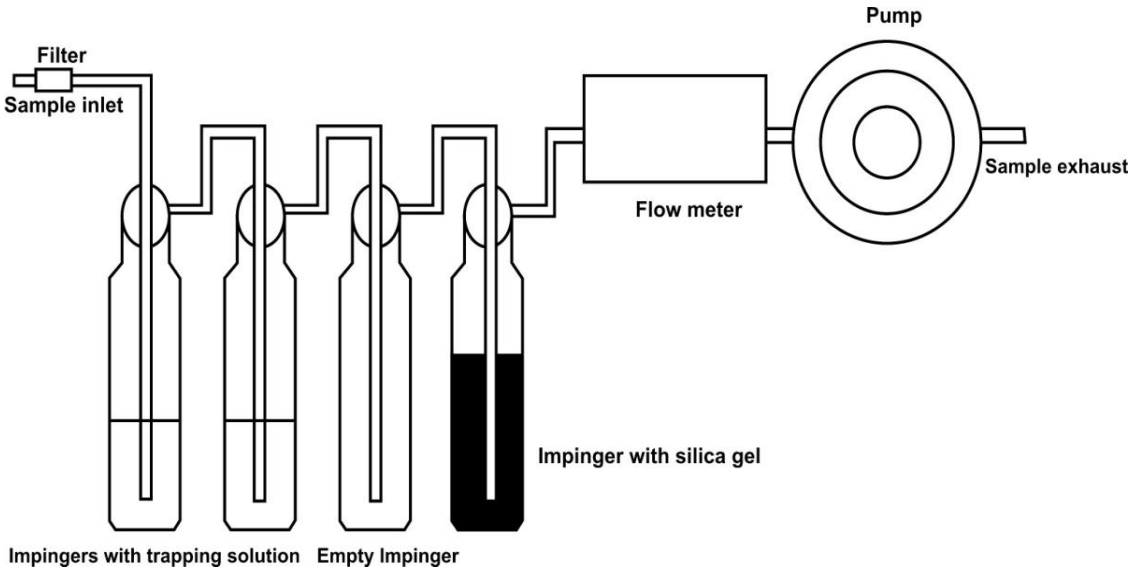

Fig. 1. Configuration of the impinger-based sampling train used in the reported studies.

Due to the low temperatures during the cold months, the impinger train was put in an ice bath to keep the acid trapping solutions from freezing. During the warm months, the impinger train was also put in an ice bath to keep the acid trapping solutions from evaporation. Upon reacting with the H_2SO_4, any amines in the air stream are converted to their sulfate salts. For most aliphatic amines, these salts are less volatile and more stable (e.g. more resistant to oxidation and chemical decomposition) than the free amine. Exact start and end times for sampling were recorded. Experimental data were recorded including locations, tube identification numbers, pump flow rates, dates, times, sampled volumes, and ambient conditions. The total volume of sampled dry gas was calculated by multiplying the average flow rate of the sampling pump by the total sampling time. The average flow rate was calculated by taking the average of flow rates before and after

sampling. After the sample was collected for the desired time, the contents of each impinger were poured into a separate 50mL amber borosilicate glass bottle (VWR, part #15900-030). Deionized water or 0.1 N H_2SO_4 was used to rinse out all interior surfaces of the two trapping solution impinger, as well as their corresponding graduated cylinder. This is done to ensure all sample residues are rinsed out and added to the respective bottles for the two impingers. All samples were placed on ice in a suitable cooler, and transported to the laboratory for analysis. Sample solutions were stored in a refrigerator (4°C) until they were analyzed, which was no later than 2 weeks after collection.

The farm being studied consisted of 12 layer houses. Two houses were selected for the study. One of the houses, designated high rise (barn 5), was 13.5 m x 158 m long and held approximately 53,800 birds. The other house, designated manure belt (barn 4), was also 13.5 m x 158 m long and held 118,700 birds. Each of the two houses has nine fans on the east side of the building and nine fans on the west side of the building. All fans are facing north and mechanically ventilated. The distance between the two selected barns is 17.5 m. A schematic layout of the sampling site was showed in Fig. 2.

The impinger sampling sites were set up in the manure barn, barn 4 (manure belt) and barn 5 (high rise) once a week. The average sampling time was typically two hours. In the manure barn, the sampling sites were set up throughout the barn to evaluate gradient concentrations of ammonia/amines. At barn 4 and barn 5, sampling sites were rotated routinely to take samples from all fans throughout the barns. Two impinger samples were taken per week, making a total of eight samples per month. A photo of the actual impinger sampling train (sampled at the north door of the manure barn, taken on October 6, 2008) was showed in Fig. 3.

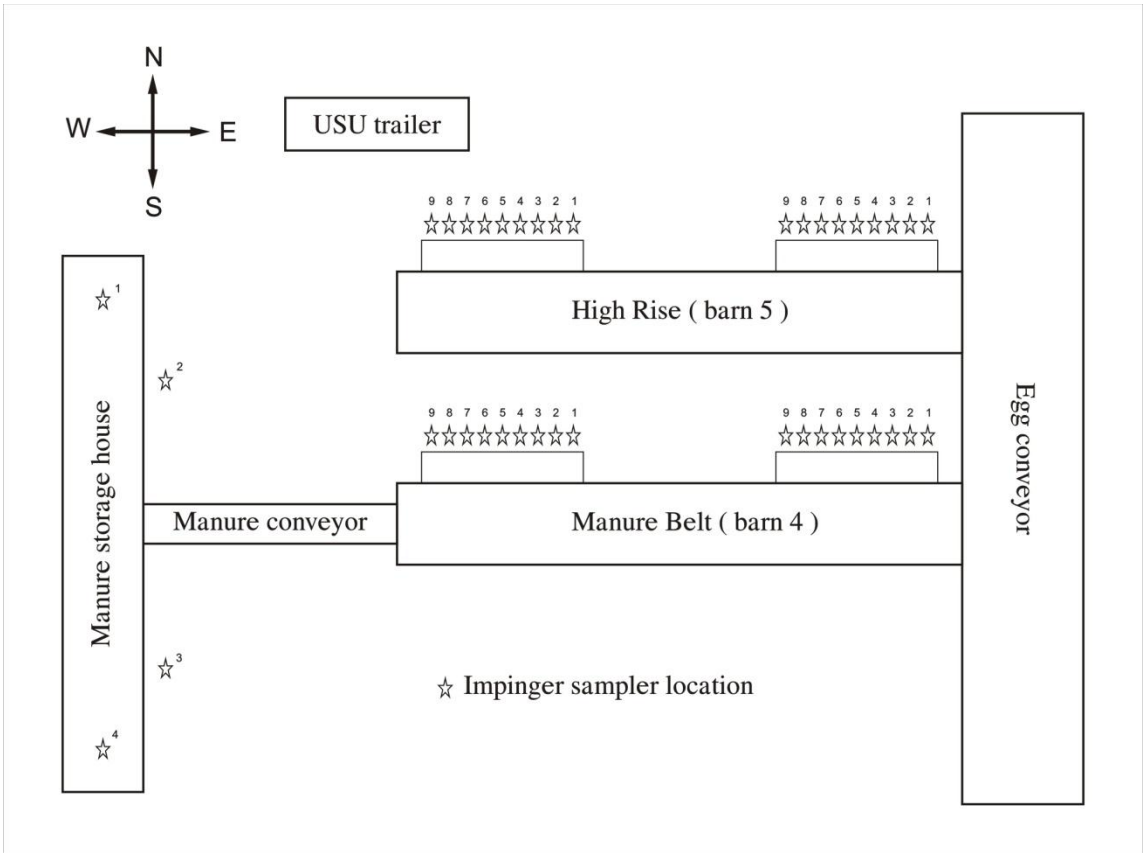

Fig. 2. A schematic drawing of the layout of the farm-sampling site.

2.2. Chemicals and reagents

All standard solutions were prepared using methylamine, dimethylamine, trimethylamine, triethylamine, n-butylamine and ammonia purchased as analytical reagent chemicals (99% purity) from Sigma-Aldrich). Methanesulfonic acid (MSA) was used as an eluent in ion chromatography (> 99% pure) was also supplied by Sigma–Aldrich. Water for chromatography was purified using a Milli-Q system (Millipore, Bedford, MA, USA) to produce 18.2 MΩ water.

Fig. 3. Impinger sampling train at north door of the manure barn on October 6th, 2008.

2.3. Instrumental Methods

The IC used in these experiments was a Dionex model ICS 1000 (Dionex Corporation, Sunnyvale, CA) equipped with electrochemical suppressed conductivity detection. The ICS 1000 integrated system performs isocratic ion chromatography (IC) separations using conductivity detection. A Dionex Cation Self-Regenerating Suppressor (CSRS ULTRA, 4 mm) was used to chemically suppress the background conductivity. Manual injections were performed using plastic syringes. The injection volume was 25 µL. Analytical grade (99.5+%, Aldrich) methanesulfonic acid (MSA) was used as the eluent in ion chromatography. The analytical column used was an IonPac CS17 (250 mm x 4 mm, I.D) and a CG17 (50 mm x 4 mm, I.D) was used as a guard column. The IonPac CS17 cation exchanger column has a hydrophilic, carboxylate functionalized stationary phase that was used for analysis of polyvalent and moderately hydrophobic amines. The ICS 1000 system was equipped with Chromeleon Chromatography Management Systems

software that controlled the IC and was used for the data analysis. The eluent flow rate was 1.0 mL/min. The methanesulfonic acid (MSA) eluent concentration was 10 mM. The current applied to the conductivity suppressor was 20 mA. The background conductivity was lower than 0.5 μS and the typical system backpressure was 1600-1700 psi.

3. Development of an IC separation method for ammonia and organic amines using a gradient elution

3.1. Standards

Standard solutions were prepared separately for each amine by diluting the pure amine standards with deionized water. For concentration calibration curves (conductivity area vs. amine concentrations), mixture solutions containing ammonia, methylamine, dimethylamine, trimethylamine, triethylamine and n-butylamine were prepared from the pure standard solutions by appropriate dilution in aqueous solutions to generate concentrations of 5, 10, 20, 30, and 40 mg/L for each of the amine standards and were subsequently stored in a refrigerator at 4ºC when not in use. New amine standards were made every six months.

3.2 Gradient elution program development

Initially, an isocratic separation of the ammonia and amines standards was developed employing MSA and water as the solvent system on the ICS 1000 system. However, it was found that a suitable separation of the organic amines could not be achieved using isocratic chromatographic conditions. The amine standards exhibited asymmetric peaks using isocratic elution conditions. Fig. 4 showed a typical separation of the standard amine mixture using isocratic solvent conditions on the ICS 1000 system using 10 mM MSA in water.

In an attempt to increase the resolution of the amine standards, the 10 mM MSA eluent was diluted first to 7 mM and then to 3 mM MSA.

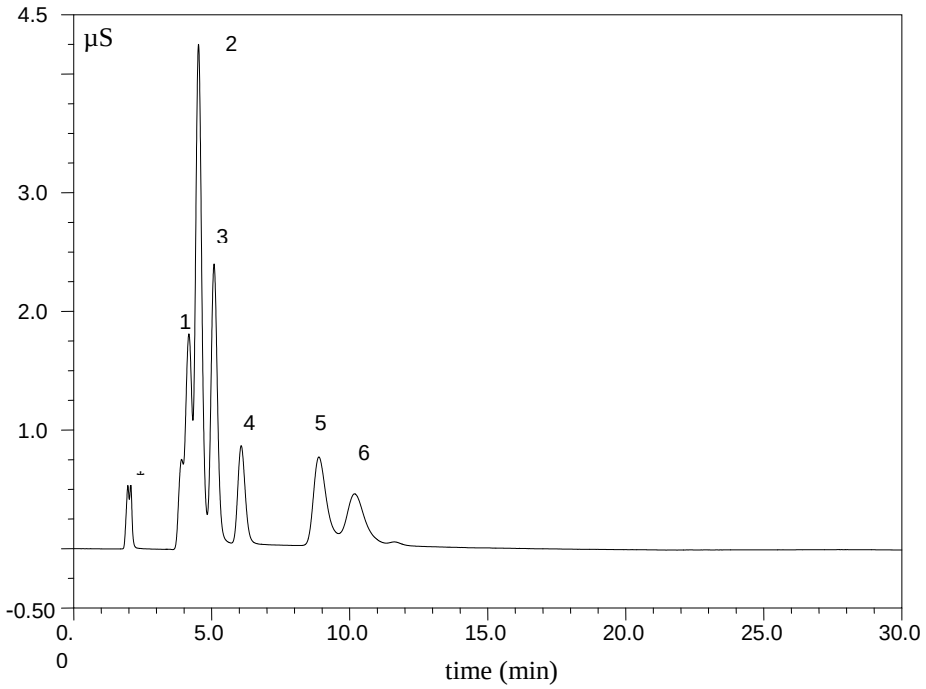

Fig. 4. Isocratic chromatogram of the standard mixture of amines * solvent peak, 1- Ammonia, 2- methylamine, 3- dimethylamine, 4- Trimethylamine, 5- n-butylamine, 6- triethylamine. Eluent : 10 mM MSA in water.

Fig. 5 and 6 showed typical chromatograms of the standard amine mixture using isocratic conditions of 7 mM MSA and 3 mM MSA. The 7 mM and 3 mM MSA mobile phase solutions give better resolution of ammonia and methylamine, but introduce significant asymmetry to the n-butylamine and triethylamine peaks.

To try to eliminate the asymmetry and tailing of the late eluting n-butylamine and triethylamine peaks, acetonitrile was added as an organic modifier to the MSA eluent in a 90:10 ratio by volume (90% of a 10 mM MSA solution/10% acetonitrile). However, the

acetonitrile modifier proved to be chemically unstable with time, as it appears to be degraded by the MSA in the solvent eluent mixture.

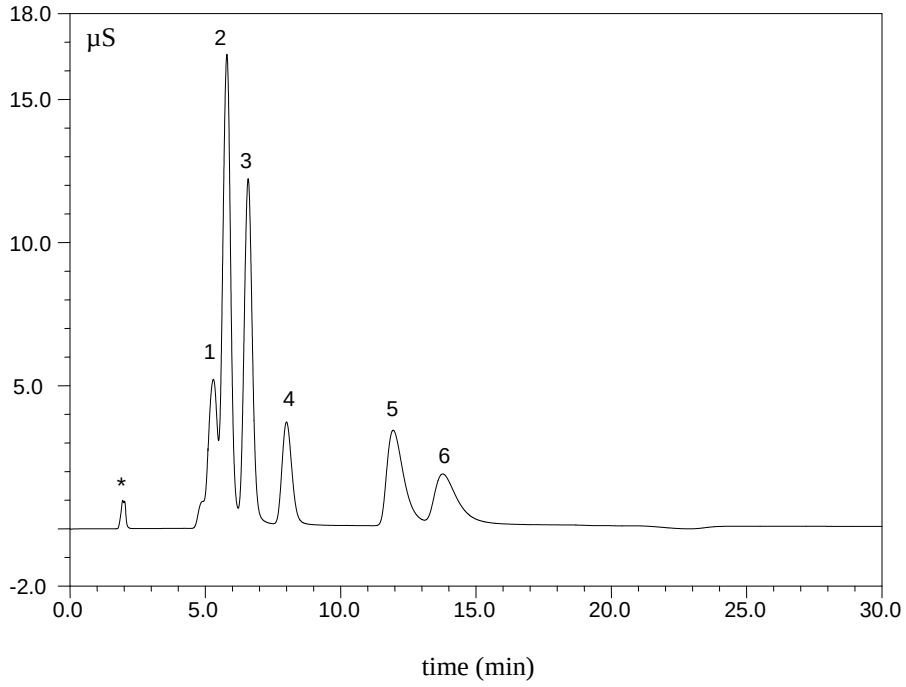

Fig. 5. Isocratic chromatogram of the standard mixture of amines * solvent peak, 1- Ammonia, 2- methylamine, 3- dimethylamine, 4- Trimethylamine, 5- n-butylamine, 6- triethylamine. Eluent : 7 mM MSA in water.

Retention times increase by as much as an additional 3 minutes for the triethylamine when the solvent mixture is left for 24 hours. Although the addition of acetonitrile improved the peak shapes substantially, the non-reproducibility of the amines elution prevented the 90% of a 10 mM MSA/10% acetonitrile from being used for the analysis. Fig. 7 and 8 show the change in elution over time when acetonitrile is mixed with MSA as the eluent for the IC.

Note that the longer elution time for the amines in Fig. 8 is believed to be due to chemical degradation of the acetonitrile with time in the highly acidic MSA effluent

solution. Decreased acetonitrile concentration would be expected to increase the elution times for the amines.

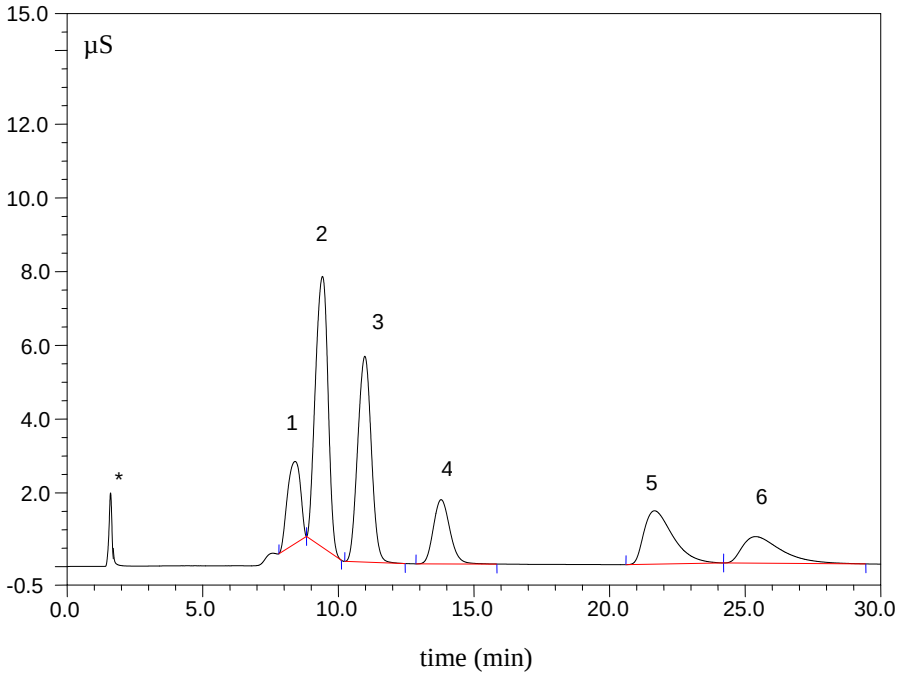

Fig. 6. Isocratic chromatogram of the standard mixture of amines * solvent peak, 1- Ammonia, 2- methylamine, 3- dimethylamine, 4- Trimethylamine, 5- n-butylamine, 6- triethylamine. Eluent : 3 mM MSA in water.

In a final attempt to improve the separation, an optimized gradient elution solvent program was developed employing 10 mM MSA and deionized water in varying compositions during the separation. To allow for a gradient program to be employed, the single pump of the ICS 1000 system was by-passed and a gradient pumping system from a series 1050 (Hewlett Packard, PA, USA) liquid chromatograph was used to provide the necessary solvent gradient for the separation of the amines standards. Fig. 9 shows the same amine mixture separated using an optimized gradient program. Fig. 9 illustrates the improvement in resolution needed for quantification of close eluting peaks by using a gradient chromatographic procedure instead of isocratic elution. The gradient program

found to be optimal was an MSA change from 20 to 80 mM MSA in 8 minutes, followed by holding at 80 mM MSA for 9 minutes.

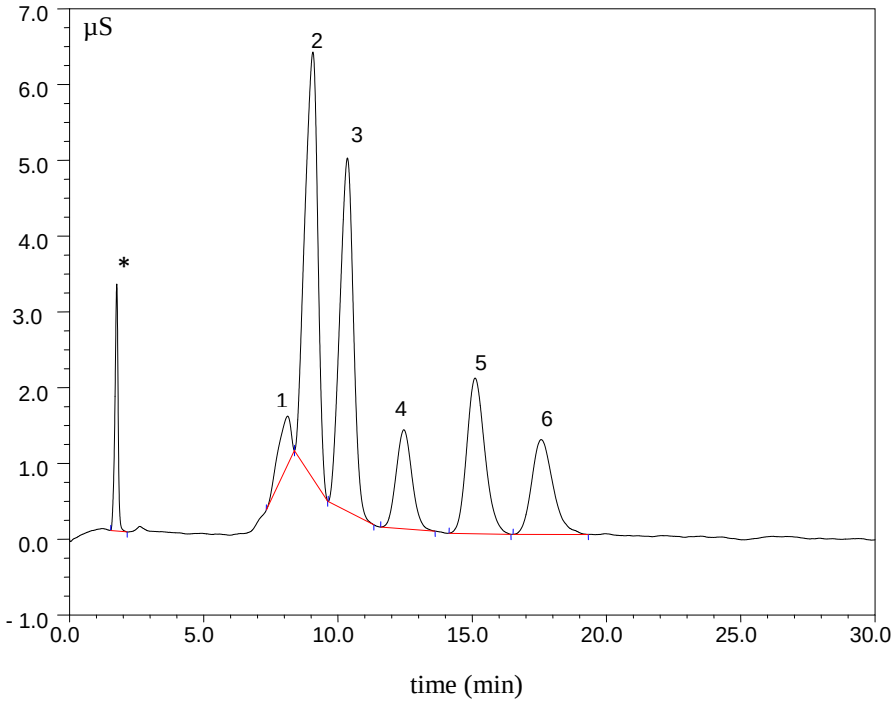

Fig. 7. Chromatogram of the standard mixture of amines; * solvent peak, 1- Ammonia, 2-Methylamine, 3- Dimethylamine, 4- Trimethylamine, 5- n-butylamine, 6-triethylamine, using freshly prepared 90% of a 10 mM MSA/10% acetonitrile as eluent.

The retention times with standard deviations (s/n=3) observed for ammonia, methylamine, dimethylamine, triethylamine, n-butylamine and triethylamine were: 7.63 ± 0.04 min, 8.09 ± 0.06 min, 8.78 ± 0.03 min, 9.89 ± 0.09 min, 12.60 ± 0.12 min and 13.78 ± 0.11 min, respectively.

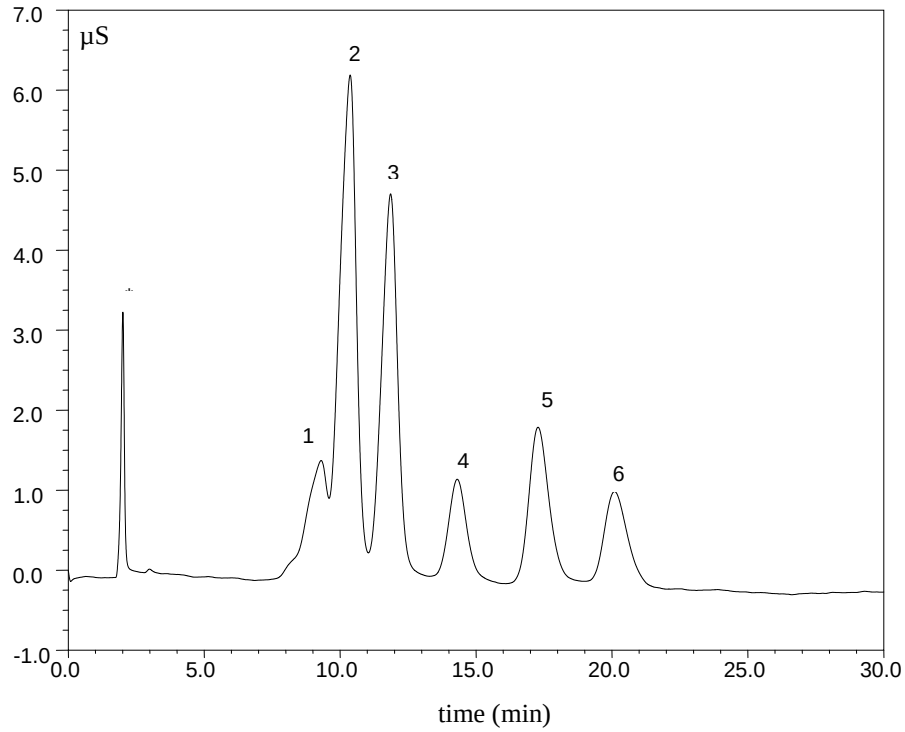

Fig. 8. Chromatogram of the standard mixture of amines; * solvent peak, 1- Ammonia, 2-Methylamine, 3- Dimethylamine, 4- Trimethylamine, 5- n-butylamine, 6- triethylamine, using 90% of a 10 mM MSA/10% acetonitrile 24 h after prepared as eluent. The degrade acetonitrile in MSA solution has shifted the amines to longer elution times.

A reverse gradient was employed over 5 minutes to return the solvent to 20 mM MSA starting conditions. The system was then re-equilibrated for 8 minutes. The flow rate employed was 1.0 ml/min and the sample injection volume used was 25 µL. The gradient program for the amines separation is shown in Table 4. The gradient elution program results in the amine standards being well separated in less than 15 minutes. The standards were run as three replicate samples using the developed gradient elution program.

One of the disadvantages of using a solvent gradient for separation is a longer analysis time. In the isocratic separation, the total analysis time was 11 minutes (with 10 mM MSA as eluent).

Table 4. Eluent program for amines separations.

Time (min)	A%	B%	Flow rate (ml/min)
0	20	80	1.00
8	80	20	1.00
17	80	20	1.00
22	20	80	1.00
30	20	80	1.00

A: 10 mM MSA in water; B: deionized water.

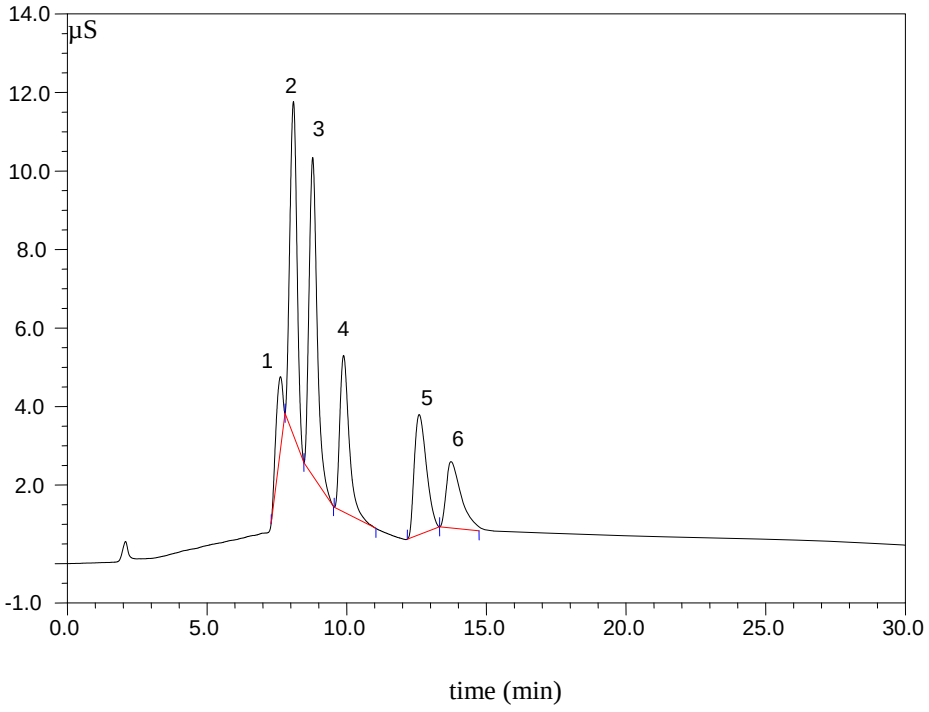

Fig. 9. Gradient chromatogram of the standard mixture of amines; * solvent peak, 1- Ammonia, 2- Methylamine, 3- Dimethylamine, 4- Trimethylamine, 5- n-butylamine, 6- triethylamine. See Table 4 for gradient conditions.

In the separation employing solvent gradient conditions, the total analysis time was 15 minutes plus the time need to re-equilibrate the column. However, the peak separation is better employing gradient relative to isocratic elution, which should improve quantitation.

4. Results and discussion

4.1 Detection limit and recovery study of organic amines

In order to determine the detection limits for the amines, each of the pure amine standard (ammonia, methylamine, dimethylamine, trimethylamine, n-butylamine and triethylamine) was spiked into a known volume of deionized water to give final concentrations in the range of 10 to 100 (mg/L). Under optimized experimental conditions (gradient conditions), all six analytes showed good linear calibration curves for the concentrations vs. area response. Limits of detection (LOD) were calculated from individual amine calibration curves using three times the average baseline noise (S/N=3) as the LOD. Detection limits of ammonia, methylamine, dimethylamine, trimethylamine, n-butylamine and triethylamine were found to be: 196, 171, 128, 98, 72 and 56 µg/L, respectively. The recoveries were between 76.8% and 88.6%. Detection limits and the recoveries (%) of the amines are listed in Table 5.

Table 5. Limit of detection and recovery percentages of analyte compounds.

Analyte	Range (ppm or mg/L)	LOD (aq) (s/n=3) (ppb)	LOD[1] (air) (ppb)	Retention Time (min)	Retention time S.D. (min)	Recovery (%)
Ammonia	10 -100	196	128	7.63	0.04	88.6
Methylamine	10 -100	171	110	8.09	0.06	82.5
Dimethylamine	10 -100	128	52	8.78	0.03	81.3
Trimethylamine	10 -100	98	27	9.89	0.09	78.8
N-butylamine	10 -100	72	19	12.60	0.12	79.1
Triethylamine	10 -100	56	11	13.78	0.11	76.8

LOD[1] see appendix C for a sample calculation.

4.2 Results of field samples

For the analysis, the collected impinge samples were first diluted with deionized water to a final volume of 50 mL for subsequent analysis (APHA, 1977). The volume of each individual amine compound in the original air sample was calculated (see Appendix A for a sample calculation):

$$V_a = (N)(0.1)(24.04)(0.001)/(FW_a) \quad (7)$$

where:

V_a = Volume of individual amine gas in the sample of gas taken from the source

N = Average concentration of amine (mg/L) in the solutions obtained from the two impingers ((Impinger 1 concentration + Impinger 2 concentration)/2)

0.1 = Conversion factor, assuming sample in each of the two impingers was each diluted to 50 mL (0.10 L total volume).

24.04 = Liters of ideal gas per mole of substance

0.001 = Factor to convert mg/L to g/L

FW_a = Formula weight of amine analyte

*: the amine concentrations from impinger 1 and 2 were calculated base on the conductivity measurements run by the IC.

All of the calculated sample volumes were subsequently corrected to standard temperature and pressure conditions (20ºC, 760 mm Hg). The volume of gas sample was corrected to standard conditions follow by the equation (see Appendix B and C for a sample of calculation):

$$V_{m(std)} = V_m(T_{std}/T_m)[(P_{bar} + \Delta H/13.6)/P_{std}] \quad (8)$$

where:

$V_{m(std)}$ = Volume of gas sample, corrected to standard conditions

V_m = Volume of gas sample

T_{std} = Standard absolute temperature, 293 K

T_m = Absolute average temperature during sampling, K

P_{bar} = Barometric pressure at the sampling site, mm Hg

P_{std} = Standard absolute pressure, 760 mm Hg

ΔH = Impinger pressure change during sampling period, mm of H_2O

13.6 = Specific gravity of mercury

The concentration (C_a, reported in ppm,) of each amine analyte present in the gas sample was calculated:

$$C_a = V_a/V_{m(std)} \times 10^6 \quad (9)$$

Using the IC method previously described, the ammonia in ambient air samples obtained at a local poultry facility in Cache Valley, UT was successfully detected and quantified. However, no organic amines were detected by the IC method in any of the collected samples. The calculated concentrations of ammonia for the various samples that

were taken are presented in Table 6 and 7. Results for samples collected each month from July 2008 to November 2009 are the average measurements of eight samples for each month. Amines were undetectable under this study. Table 6 shows the concentrations of ammonia detected in barn 5 and Table 7 shows the concentrations of ammonia detected in barn 4. The uncertainties of each month are the standard deviations of total of four samples.

Table 6. Concentrations of ammonia from 07/2008 to 11/2009 at barn 5 (high rise).

Month	Concentration of NH_3 in the impinger solution (ppm)	Air Concentration of NH_3 in Barn 5 (ppm) (not corrected for % recovery)	Air Concentration of NH_3 in Barn 5 (ppm) (corrected for % recovery)
Jul-08	30.1 ± 2.9	11.9 ± 2.3	13.4 ± 2.3
Aug-08	32.6 ± 2.4	13.7 ± 2.1	15.5 ± 2.1
Sep-08	29.3 ± 2.6	13.9 ± 2.0	15.7 ± 2.9
Oct-08	23.7 ± 3.6	13.2 ± 3.1	14.9 ± 3.1
Nov-08	23.9 ± 2.1	10.3 ± 2.4	11.6 ± 2.4
Dec-08	18.5 ± 2.2	8.4 ± 2.1	9.5 ± 2.1
Jan-09	17.3 ± 2.5	7.9 ± 2.1	8.8 ± 2.1
Feb-09	15.2 ± 2.4	6.5 ± 2.3	7.3 ± 2.3
Mar-09	16 ± 2.8	6.6 ± 2.1	7.4 ± 2.1
Apr-09	19.5 ± 1.8	9.7 ± 2.1	10.9 ± 2.1
May-09	21.6 ± 2.7	9.9 ± 2.2	11.2 ± 2.2
Jun-09	31.2 ± 3.8	13.8 ± 2.7	15.6 ± 2.7
Jul-09	29.1 ± 3.6	14.0 ± 2.9	15.8 ± 2.9
Aug-09	31.6 ± 3.6	14.6 ± 3.4	16.2 ± 3.4
Sep-09	27.1 ± 2.6	13.9 ± 2.2	15.7 ± 2.2
Oct-09	27.4 ± 3.8	10.7 ± 3.2	12.1 ± 3.2
Nov-09	19.7 ± 2.8	8.8 ± 2.9	9.9 ± 2.9
Minimum	15.2 ± 2.4	6.5 ± 2.3	7.3 ± 2.3
Maximum	31.6 ± 3.6	14.6 ± 3.4	16.2 ± 3.4
Average	24.7 ± 5.8	11.3 ± 3.5	12.7 ± 3.1
SD	5.8	3.5	3.1

For high rise barn (barn 5), the maximum concentration value of 16.2 ± 3.4 ppm of ammonia was detected in the month of August and the minimum value of 7.3 ± 2.3 ppm was occurred in February. The standard deviation was 5.8 ppm for concentration in aqueous and 3.1 ppm for concentration in ambient air. For manure belt (barn 4), the maximum concentration value of 15.8 ± 2.4 ppm of ammonia was detected in the month of September and the minimum value of 6.9 ± 2.0 ppm was occurred in January. The standard deviation was 5.1 ppm for concentration in aqueous and 2.9 ppm for concentration in ambient air.

The yearly average of ammonia concentration is 11.9 ± 2.9 ppm for the manure belt and 12.7 ± 3.1 ppm for the high rise. The higher temperature in the warm months favors the volatility of ammonia, thus given higher values of ammonia concentrations in the summer.

On February 10th, 2009, the impinger samplers were set to sample air at east fan # 1 and west fan # 9 of barn 4 (the two ends of barn 4). The determined concentrations of ammonia were 6.9 ppm for east fan # 1 and 7.8 ppm for west fan # 9. On August 25th, 2009, the impinger samplers were set to sample air at the same fans (east fan # 1 and west fan # 9) of barn 4. The concentrations of ammonia were calculated at 12.9 ppm for east fan # 1 and 11.6 ppm for west fan # 9. The higher concentrations of ammonia in August compared to February at barn 4 are due to the higher temperature during the summer, thus favored the higher emission of ammonia. On February 24th, 2009, the impinger samplers were set to sample air at east fan # 1 and west fan # 9 of barn 5 (the two ends of barn 5). The determined concentrations of ammonia were 7.2 ppm for east fan # 1 and 6.1 ppm for west fan # 9. On July 21st, 2009, the impinger samplers were set to sample air at

the same fans (east fan # 1 and west fan # 9) of barn 5. The concentrations of ammonia were calculated at 14.3 ppm for east fan # 1 and 13.7 ppm for west fan # 9. The higher concentrations of ammonia in July compared to February at barn 5 are due to the higher temperature during the summer, thus favored the higher emission of ammonia. The monthly average values from July 2008 to November 2009 of NH_3 concentrations in air were showed in Fig. 10.

Table 7. Concentrations of ammonia from 07/2008 to 11/2009 at barn 4 (manure belt).

Month	Concentration of NH_3 in the impinger solution (ppm)	Air Concentration of NH_3 in Barn 5(ppm) (non corrected with recovery)	Original Air Concentration of NH_3 in Barn 5(ppm) after corrections of recovery
Jul-08	25.6 ± 3.6	10.2 ± 2.1	11.5 ± 2.1
Aug-08	28.5 ± 2.9	12.0 ± 2.4	13.5 ± 2.4
Sep-08	29.6 ± 2.5	14.0 ± 2.9	15.8 ± 2.9
Oct-08	24.6 ± 2.8	13.8 ± 2.5	15.6 ± 2.5
Nov-08	22.7 ± 3.2	9.7 ± 2.2	11 ± 2.2
Dec-08	19.8 ± 2.6	9.3 ± 2.1	10.2 ± 2.1
Jan-09	13.6 ± 2.8	6.1 ± 2.0	6.9 ± 2.0
Feb-09	15.2 ± 2.4	6.5 ± 1.8	7.3 ± 1.8
Mar-09	17.3 ± 2.1	7.1 ± 2.1	8 ± 2.1
Apr-09	18.2 ± 2.3	9.0 ± 2.4	10.2 ± 2.4
May-09	20.8 ± 2.8	9.5 ± 1.6	10.7 ± 1.6
Jun-09	30.7 ± 3.1	13.7 ± 2.3	15.5 ± 2.3
Jul-09	29.2 ± 3.3	13.8 ± 2.4	15.6 ± 2.4
Aug-09	25.6 ± 3.0	11.6 ± 3.1	13.1 ± 3.1
Sep-09	24.9 ± 2.4	12.7 ± 3.5	14.4 ± 3.5
Oct-09	25.6 ± 3.5	10.0 ± 3.4	11.3 ± 3.4
Nov-09	21.4 ±3.9	9.6 ± 2.9	10.8 ± 2.9
Minimum	13.6 ± 2.8	6.1 ± 2.0	6.9 ± 2.0
Maximum	30.7 ± 3.1	14.0 ± 2.9	15.8 ± 2.4
Average	23.2 ± 5.1	10.5. ± 3.2	11.9 ± 2.9
SD	5.1	3.2	2.9

Fig. 11 shows a representative chromatogram of a typical field sample (collected on 04/15/2009) that only showed a chromatographic peak for ammonia. The analyte retention time of this peak was 7.61 min. No organic amines are detected under in any of the collected air samples during the study period using the developed IC procedure.

For comparison, a photoacoustic field gas monitor (Innova model 1412, Thermo Scientific, Waltham, MA) was used to measure the concentrations of ammonia gas at the same poultry facility. The photoacoustic field gas monitor selectively measures a wide range of gases/vapor; NH_3, EtOH, CO_2, N_2O and H_2O. A vacuum pump connected to Teflon tubing sucks the inside barn air form each sampling location and passes it through the Innova 1412 which directly detects the concentration of the gases.

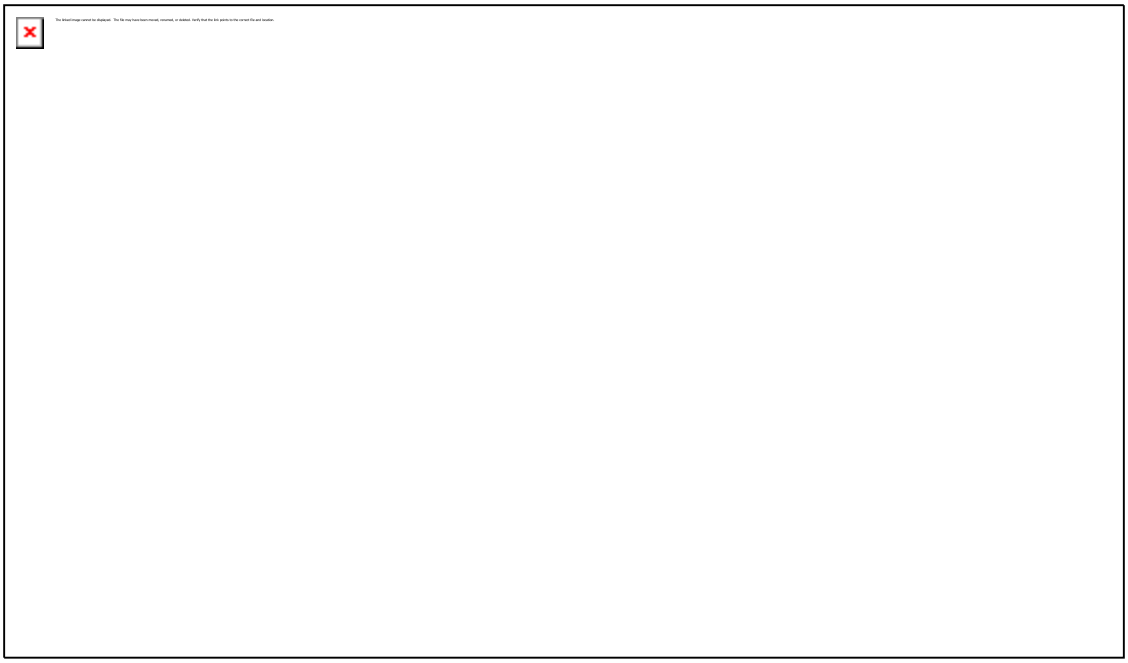

Fig. 10. Ammonia concentrations in air detected by IC with standard deviations of 4 samples of each month.

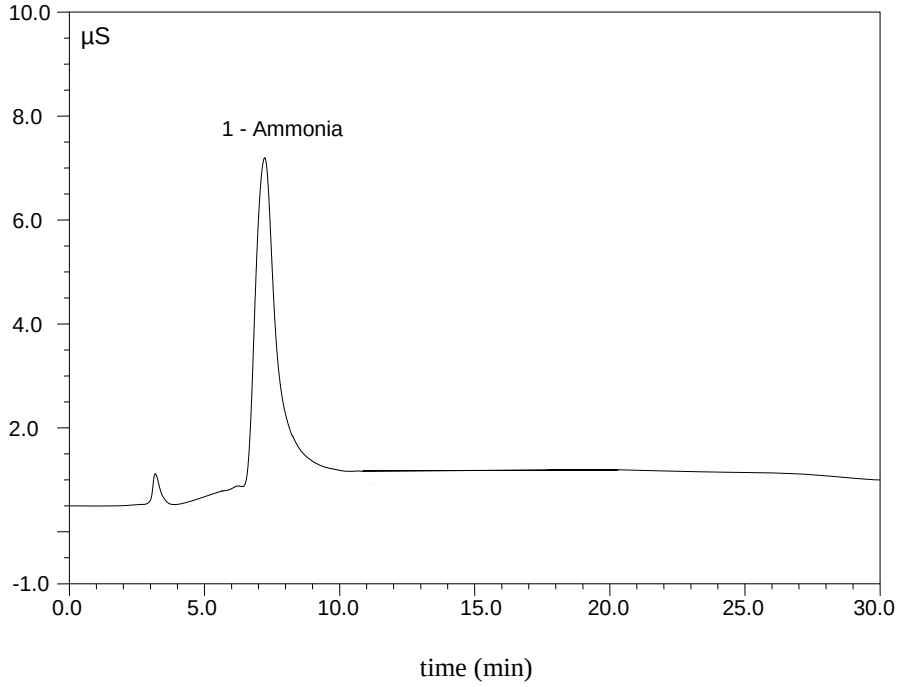

Fig. 11. A chromatogram of a field sample (collected on 02/23/2009) that contains ammonia.

According to data recorded on September 17th 2008, the measured ammonia gas concentrations typically ranged from 5.31 to 15.47 ppm over 24 hour period with a mean concentration of 11.62 ± 0.89 ppm in the exhausted air from the high-rise building (barn 5) (Ogunlaja, 2008). Using the IC method (Table 6), the concentration of ammonia (for 2 hour measurement) for the month of September was observed 15.7 ± 2.9 ppm. In Ogunlaja's study (Ogunlaja, 2008), the yearly average concentration of ammonia measured by the photo acoustic field gas monitor was reported as 11.2 ± 0.75 ppm. Using the IC method in this study, the yearly ammonia concentrations ranged from 7.3 to 16.2 ppm with a mean of 12.7 ± 3.1 ppm. Taking the error into the account and differences in total sampling times, the two yearly average results were very similar in term of the

measured concentrations of ammonia in air. This suggests that the impinger sampling train method with the IC detection was comparable to the photo acoustic field gas monitor. The advantages of the photo acoustic field gas monitor were its simplicity and require no sample preparation. It provided real-time data and requires no additional analysis time when compared to the IC method. It does not, however, differentiate between organic amines and NH_3, which was a major goal of the study. The IC method can also provide a validation of the photo acoustic field gas monitor measurements.

Because there were no amines detected by the IC method, another study was conducted to determine if the organic amines are not being observed because they have too low a vapor pressure to be sampled efficiently by the impinger or if they are trapped as salts within the manure, or are of too low a concentration to be observed by the IC method. Alternately, they may simply not be present in the sample. To test these possibilities, a representative composite manure sample was generated by mixing four samples of manure sampled from October and November of 2009 (two samples of each month). The composite manure was used in the following experiments.

To test for the possibility that organic amines in the manure were tied up as low volatility salts within the manure, the pH of a composite manure sample was raised to approximately a pH of 9 by adding NaOH to the manure to convert any organic amines to the free bases. Approximately 20 grams of composite manure was placed into an Erlenmeyer flask and the flask was connected with the impinger sampling train for air sampling. After 2 hours for air sampling, no organic amines were detected.

To further test for possibility that organic amines had too low a vapor pressure to be effectively sampled by the impinger method, approximately 20 grams of the

composite manure sample was placed into an Erlenmeyer flask and the Erlenmeyer flask was heated. A known volume of air was passed through the Erlenmeyer flask to transport any volatile amines to the impingers sampling train for trapping. Fig. 12 shows the set up of the experiment. The sample was run at room temperature and was heated up approximately to 30 ºC, 40 ºC and 50 ºC, respectively. By increasing the temperature of the samples, it will increase the volatility of any amines compounds present and allow them to be trapped by the acid solution in the impingers. No organic amines were detected in the composite manure sample by increasing the sample's temperature.

Results for samples collected using these two experiments are shown in Fig. 13a and 13b. Fig. 13a is a chromatogram of a composite manure sample that was heated to 40 ºC. Fig. 13b is a chromatogram of a composite manure sample that was adjusted to pH 9.

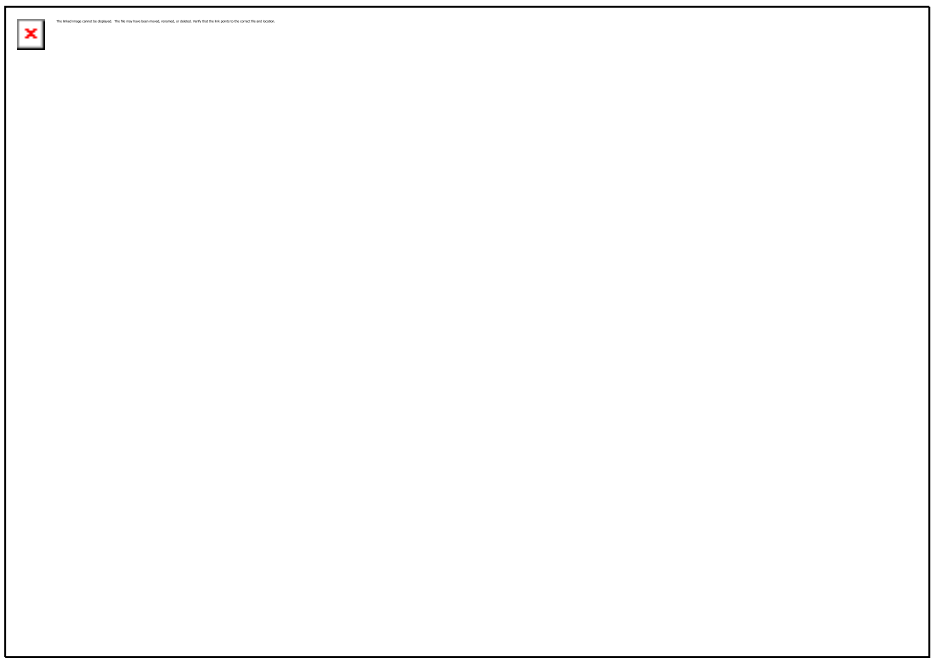

Fig. 12. A composite manure sample was heated up to different temperatures (30 ºC, 40 ºC and 50 ºC) and was sampled with the impinger train.

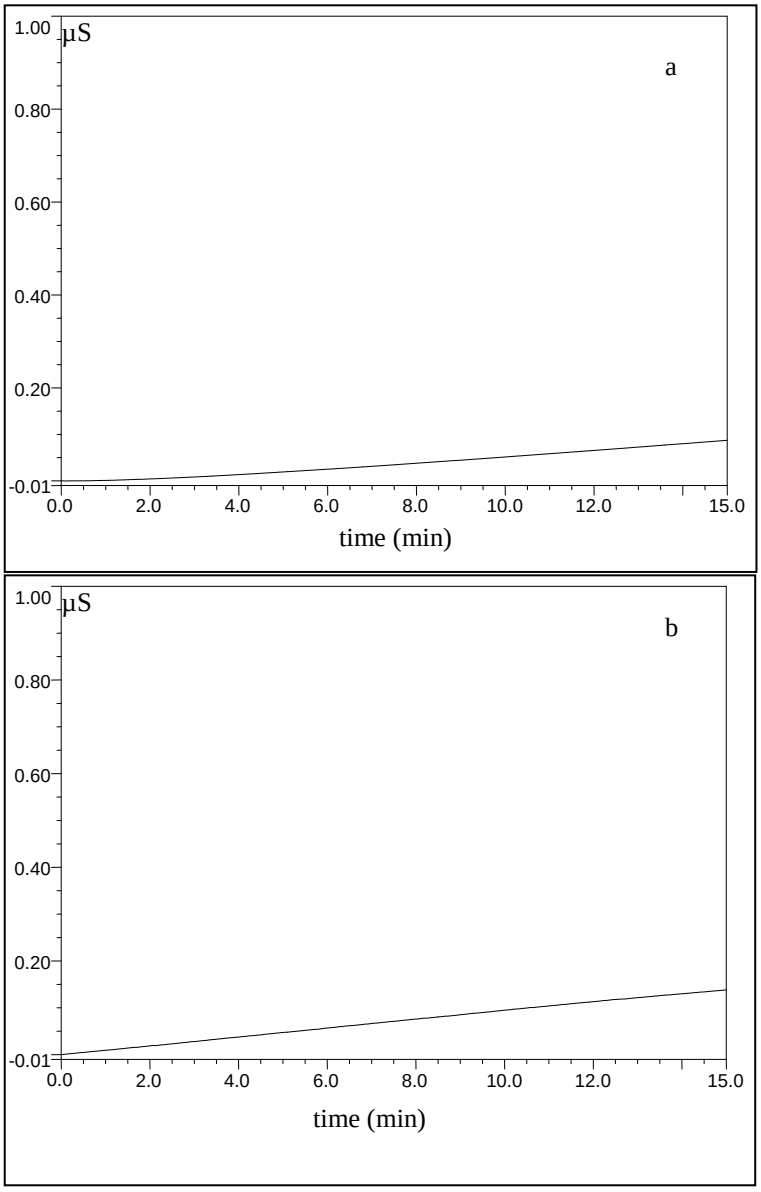

Fig. 13. a) Chromatogram of a composite manure sample, heated to 40ºC. b) Chromatogram of a composite manure sample adjusted to pH 9.0.

To test the efficiency of trapping organic amines with the impingers and to study the actual detection limits of organic amines in the manure, the composite manure sample was spiked with known amounts of the standard amines and an impinger sampling train was set up to sample the room temperature air above the spiked manure sample.

Approximately 20 grams of the composite manure sample that was spiked with 1 ml of standard amine was placed into an Erlenmeyer flask and the Erlenmeyer flask was connected into an impinger sampling train. Spiked concentrations of amine standards studied were: 40 ppm, 30 ppm, 20 ppm and 10 ppm.

Results from the IC showed the impinger successfully trapped the higher levels of the amines when their concentration was above 20 ppm. The detection limit of the added amines to the manure sample was between 10 ppm and 20 ppm as no amine peaks were observed for the 10 ppm spike sample. Fig. 14 showed the spiking 30 ppm result.

A 30 ppm spiking solutions into the composite manure was approximately 1.5 ppm of pure organic amines (30 μg/20 g). Using conductivity and peak areas from the chromatogram, the concentration of methylamine detected in the spiked manure sample was calculated at 9.4 ppm, which represents about 31% trapping efficiency (30 ppm spiked in vs. 9.4 ppm recovered). The calculated recovery concentrations for dimethylamine, trimethylamine, n-butylamine and triethylamine were 6.3 ppm, 4.9 ppm, 4.1 ppm and 2.4 ppm, respectively. The trapping efficiency for dimethylamine, trimethylamine, n-butylamine and triethylamine were 21%, 16%, 13% and 8%, respectively.

This is consistent with the relative volatility of the amine standards. At the 10 ppm spiking level, no measureable amount of organic amines were seen. This would indicate that at lower concentrations, much of the organic amines, if present, are bound up in the manure sample and not volatile. Bases upon these spiking experiments, the organic amines in the manure must occur at a minimum concentration of 1 ppm

(20µg/20g) in order to have sufficient vapor pressure so that enough is transported to the impingers for trapping and subsequently be detected by the IC.

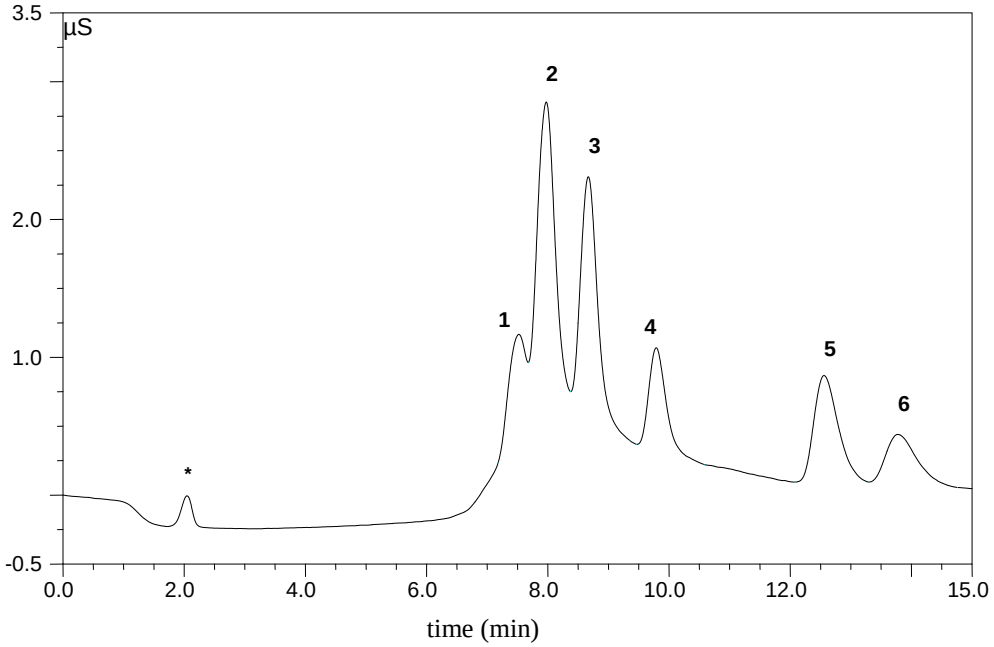

Fig. 14. A chromatogram of spiking manure with 30 ppm amines mixture. * solvent peak, 1-ammonia, 2-methylamine, 3-dimethylamine, 4-trimethylamine, 5-n-butylamine, 6-triethylamine.

5. Conclusions

By using impinger bubbling as a sampling method, ammonia was successfully detected and quantified using ion chromatography and ion conductivity detection. The yearly average concentration from July 2008 to November 2009 of ammonia in ambient air at the barns was calculated at 11.9 ± 2.9 ppm at the manure belt barn and 12.7 ± 3.1 ppm at the high rise barn. No organic amines in the collected ambient air samples were detected, possibly due to the low concentration that prevented the amines from having sufficient vapor pressure to be sampled by the impinger method. Thus, the hypothesis of significant concentrations of organic amines being present in ambient air in the various

barns is invalid. Comparison of the developed IC method with measurements made using a photo acoustic field gas monitor in another study showed that the two methods measured similar of ammonia concentrations in the ambient air. Further studies to determine if any organic amines are tide-up within the manure as non-volatile species (chemisorbed or physisorbed to the manure) will require an alternate analysis method. One approach to answering this question might involve using solvent extraction of the manure samples, followed by ion chromatography.

CHAPTER 3

DETERMINING TOTAL KJELDAHL NITROGEN AND AMMONIA CONTENT AND NITROGEN BALANCE FROM A CONFINED POULTRY FACILITY

1. Introduction

One of the biggest estimated sources of ammonia in the environment is from agriculture related sources, including beef and dairy cattle, swine, and poultry. Emissions from these sources have been quantified in Europe using emission factors which reflect the environment of the agriculture facility (Faulkner and Shaw, 2008). These factors can be in kg NH_3 $animal^{-1}$ $year^{-1}$ or mg NH_3 $animal^{-1}$ day^{-1} and can be used to calculate the ammonia emissions for a facility if the number of animals is known. To date, limited information has been reported concerning ammonia emission from agriculture in the U.S. system (Burns et al., 2003). However, researchers are just beginning to quantify ammonia emissions from animal housing facilities as government agencies and concerned citizens become more concerned about emissions in recent years (NAS, 2002). Emission factors specific to the U.S. must be determined in order to quantify ammonia emissions from agriculture facilities. Once values for the source of ammonia emissions are obtained, then the focus can turn to reducing these emissions.

The ammonia levels and resulting emissions during the handling of manure within animal-production facilities have significant health and environmental impacts. Ammonia (NH_3) has been identified as one of the important noxious gases emitted by large animal facilities (Lim et al., 2006). Thus quantification of NH_3 emission from such facilities is needed. In addition, the total nitrogen is an important manure property that affects emission of ammonia and other nitrogen containing compounds (USEPA, 2001a).

As described in Chapter 1, the emission from a local facility located in Cache Country, Utah was studied by analyzing the ammonia content and total Kjeldahl nitrogen (TKN) of animal production and waste, as well as calculating the nitrogen loss to the atmosphere. In order to experimentally measure the amount of nitrogen released into the atmosphere as ammonia, TKN values were obtained weekly for animal feed, eggs and manure. The difference between the amount that entered the chicken in their feed, and that exited the chicken in their eggs and manure, correlated to the amount of ammonia released from the manure. These calculated values were the emission factors. In addition to the TKN and NH_3-N analysis, the pH and moisture content of samples were also measured to further analyzing the nitrogen emission.

2. Experimental section

2.1. Sampling

Chicken manures were sampled at three different barns in the livestock facility at manure barn, barn 4 (was run with a conveyer belt) and barn 5 (high rise). The manure barn held the older manure from barn 4. Within barn 4 with the manure was being removed from the housing barn via the manure belt system. Barn 5 employed a manure storage method in which the manure and urine are stored together in a pit beneath the housing level. Several sub-samples of chicken manure were taken to produce a composite sample. Due to the plentiful litter and animal feathers, sampling was conducted using a shovel. Manure was collected by scooping into a bucket from several random locations in the manure pile and then mixing them in the bucket. Manure was stored in Ziploc bags. Manure alone with the animal feed and eggs, which were provided by the farm manager, were collected weekly from May 2008 to November 2009. After collecting, manure, feed

and egg samples were transported to the laboratory and stored in the refrigerator at 4 ºC prior to the analysis (USEPA, 2001b).

2.2. Reagents and materials

The reagents used in this experiment are concentrated sulfuric acid H_2SO_4 (18 M), concentrated sodium hydroxide NaOH (40% w/w), propac powder, saturated boric acid solution with indicator, acetyl tributyl citrate 99% pure (purchased from Acros Organic). All reagents were of analytical grade. The digestion and distillation for the experimental apparatus were bought from Labconco, with the block heater and 800 mL Kjeldahl flasks.

2.3. Total Kjeldahl nitrogen analysis

The Kjeldahl method for nitrogen analysis is composed of three distinct steps. These are digestion, distillation, and titration. Chemical reactions of the TKN method were showed below:

$$\text{Organic N} + H_2SO_4 \rightarrow (NH_4)_2SO_4 + H_2O + CO_2 \quad (10)$$

$$(NH_4)_2SO_4 + 2NaOH \rightarrow 2NH_3 + Na_2SO_4 + 2H_2O \quad (11)$$

$$NH_3 + H_3BO_3 \rightarrow NH_4^+H_2BO_3^- \quad (12)$$

The purpose of the digestion step is to break the intricate structure and chemical bonds that hold a chemical substance down to simple chemicals and ionic structures. The sample is first digested in strong sulfuric acid in the presence of a catalyst (equation 10), which helped in the conversion of the amine nitrogen to ammonium ions (USEPA, 2001a). To accomplish this, one to two grams of the samples (manure, feed or egg) were placed into an 800 mL Kjeldahl flask with 25 mL of concentrated sulfuric acid (H_2SO_4). About 15 g of propac powder, which contained copper and potassium sulfate, was added into the flask to act as a catalyst and to increase the boiling point of the acid so as to

decrease the time needed for digestion. The digestion tube was placed into a digestion block where it was heated to the boiling temperature of the mixture. The temperature was maintained at 150 °C for 1 h, and then, at 400 °C for 2 h. Digestion was usually completed after a total of three hours. Fig. 15 shows a picture of the digestion apparatus before the sample broke down into the ammonium sulfate $(NH_4)_2SO_4$.

Fig. 15. Digestion apparatus during the digestion.

After all of the inorganic species in the sample has been converted to ammonium sulfate $(NH_4)_2SO_4$, the samples changed from black to clear greenish color as shown in Fig. 16. Blank solutions were analyzed in the same way, and their measurements were considered to determine the nitrogen concentrations in the samples.

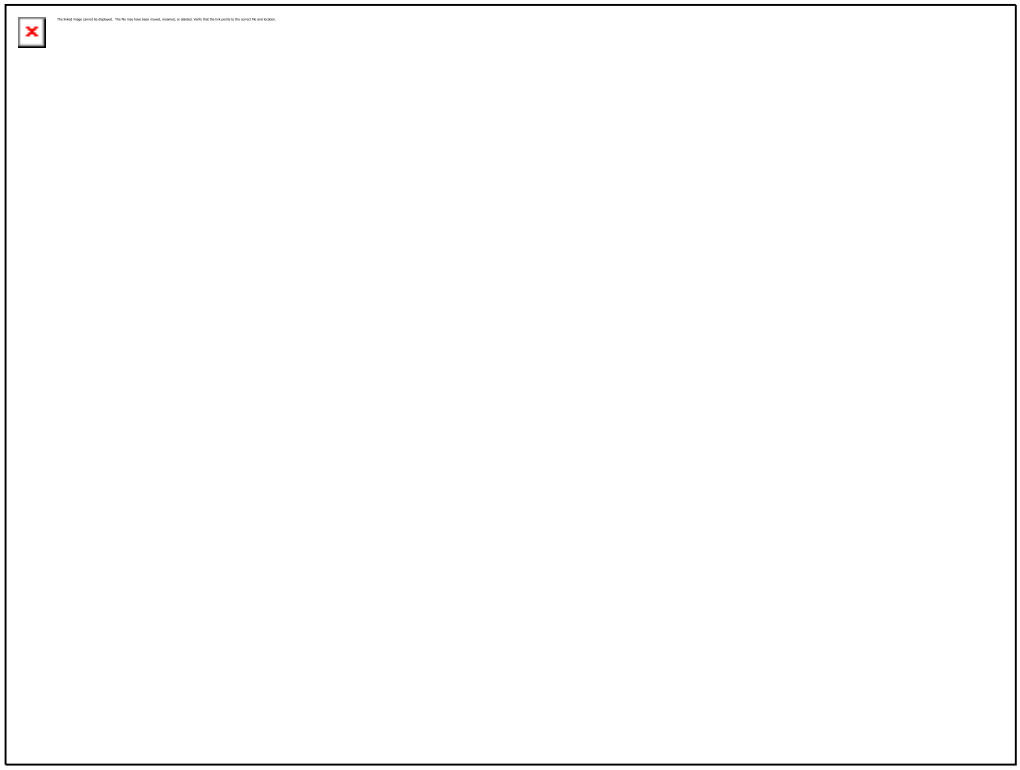

Fig. 16. Digestion apparatus after the digestion has been completed.

After the sample has been completely digested, it was set aside to cool to room temperature for about an hour before continuing to the distillation step. Distillation involves the separation of ammonia – nitrogen from the digestate. After the sample has been cooled to room temperature, water (300 mL), acetyl tributyl citrate (defoamer, 4-5 drops) and sodium hydroxide NaOH (60 mL) were added to form Na_2SO_4, H_2O and NH_3 (see equation 11). Glass beads were also added to reduce excess boiling. The purpose of adding NaOH was to convert ammonium (NH_4^+) ion to ammonia (NH_3) so that it was possible to separate the nitrogen by distilling the ammonia and collecting the distillate in a suitable trapping solution. In this study, the trapping solution was used was boric acid (Kjelsorb solution, 100 mL) with color indicator. The water and NH_3 (200 mL) were

distilled into a boric acid solution as shown in Fig. 17. The ammonia was bound to the boric acid in the form of ammonium borate (equation 12).

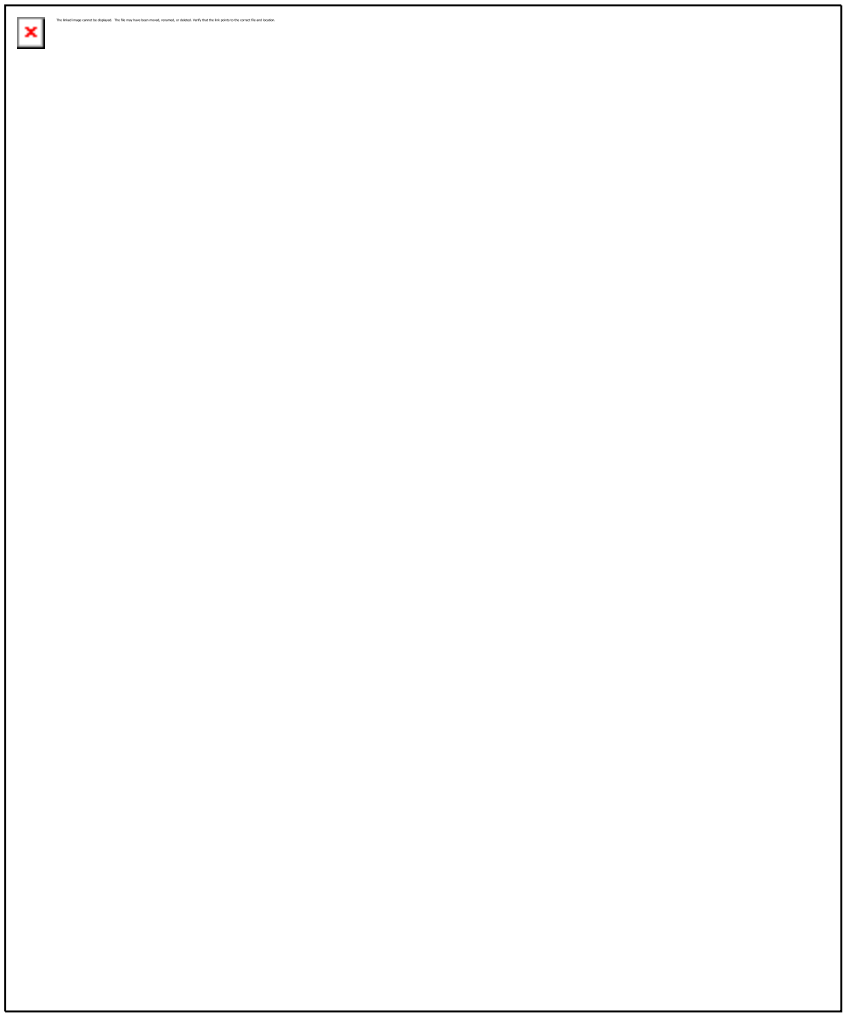

Fig. 17. Distillation apparatus.

After the sample had been with distilled, it was back titrated with standardized dilute sulfuric acid (0.1 N H_2SO_4). The volume of the acid required for the back titration was then used to determine the nitrogen content of the sample. A nitrogen containing standard (EDTA disodium dihydrate) was also tested using the same procedures within 12 hours of the samples to ensure that the results were reliable.

The amount of total Kjeldahl Nitrogen (TKN) (in units of % N) in the samples was calculated (see Appendix D for a sample of calculation) as follow:

$$TKN = [Titrant_{sample} / \text{sample weight (g)}] \times H_2SO_4 \text{ normality} \times 1.4007 \quad (13)$$

2.4. Ammonia content analysis

This method was nearly identical to the TKN method, except the sample was not digested. The ammonia in a manure sample is distilled away from the rest of the sample, at which point it is captured in a dilute boric acid solution which contains a bromocresol green methyl red indicator. The ammonia concentration of the distillate was then determined by titration with sulfuric acid (Bremner and Keeney, 1965). The procedure started from the addition of the water (50 mL for standard, 200 mL for samples), defoamer, and sodium hydroxide to the sample (about 2 gram of manure). Because a smaller amount of water was used, only 50 mL was distilled and collected for the standards, and only 150 mL were distilled and collected for the samples. The distilled samples were greenish clear and were titrated with 0.1 N H_2SO_4 to back calculate the ammonia content. The equivalent point was a dark purple color. This procedure quantified only the nitrogen originally present in the sample as ammonia. This analysis was only done on manure samples and has been validated by titration of an ammonium chloride standard.

Similar to the calculation for TKN, the NH_3-N (in unit mg NH_3/g_{manure}) in the samples was calculated (see Appendix E for a sample of calculation) as follow:

$$NH_3\text{-}N = [Titrant_{sample}\,(mL) / \text{sample weight (g)}] \times H_2SO_4 \text{ normality} \times 1.4007 \quad (14)$$

3. Nitrogen balance calculation

An ammonia-nitrogen (NH_3-N) balance for a livestock housing facility can provide a check for airborne ammonia emissions that were calculated based on measured air NH_3-N concentrations in the building's air exchange system (Keener et al., 2002). NH_3-N losses were estimated using a mass balance approach (Keener et al., 2002). Nitrogen concentrations of all materials, including animal flesh and production entering and leaving the monitored housing facility need to be determined or estimated. Nitrogen balances for animal-production systems enable prediction of upper limits on NH_3 emission (Keener and Zhao, 2008). Fig. 18 was a schematic of an animal-production system viewed as a controlled system with input and outputs (Keener and Michel, 2005; Keener and Zhao, 2008). The schematic was generalized for the case of body growth, milk and egg production. Analysis of this production system for NH_3-N assumed no other gaseous losses of N.

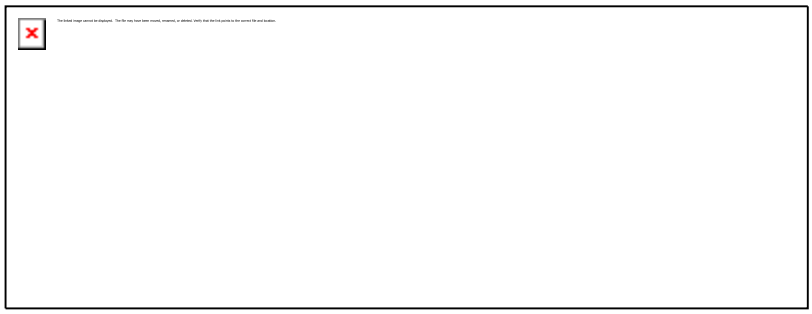

Fig. 18. Schematic of an animal production system with input, and output variables (Keener and Zhao, 2008).

The daily N fluxes in inputs (feed) and outputs (eggs) were calculated (see Appendix F for a sample of calculation) as follows:

Daily nitrogen flux (NF) in feed (mg/bird-day)

$$NF_{feed} = R_{Nfeed} * m'_{feed} / n_b \quad (15)$$

Daily nitrogen flux (NF) in eggs (mg/bird-day)

$$NF_{egg} = m_{egg} * \zeta_{egg} * R_{Negg} \quad (16)$$

Total nitrogen flux (NF) in manure (mg/bird-day) was determined according to:

$$NF_{man} = R_{N:man} * w_{man} \quad (17)$$

The NH_3 an emission per manure storage period was calculated as followed:

$$EM_{NH3} = (NF_{feed} - NF_{egg} - NF_{Dman}) \times 1.2143 \quad (18)$$

where:

R_{Nfeed} (mg/g) = TKN content of feed

m'_{feed} (kg/barn-day) = Daily feed consumption rate

n_b (birds/barn) = Number of animals

m_{egg} (g) = Average egg mass

ζ_{egg} (egg/bird-day) = Production egg efficiency (obtained from farm manager)

R_{Negg} (mg/g) = TKN content of egg

$R_{N:man}$ (mg/g) = TKN content of manure

w_{man} (tons/barn) = Manure production rate (obtained from farm manager)

1.2143 is used to convert molar mass of N to molar mass of NH_3

Manure composition significantly affects its emission of odor and individual chemical components. Therefore, the solids-to-liquids ratio of manure was an important property to be measured. Moisture content of manure has a major effect on NH_3 release from the manure (Liang et al., 2005). Higher moisture content results in a higher ratio of

NH_3/TKN_{Manure} in the stored manure, which result in a higher percentage of N loss (National Research Council, 2003). In this study, the pH of samples was taken in addition to the analysis of the moisture content of all the samples. To analyze for the moisture content, a well mixed sample aliquot, having a wet weight between 25 and 50 g, was dried in the oven at 103 ºC to 105 ºC in order to drive off all of the water in the sample. This step allowed for the determination of total solids. Following cooling, the total solid portion of the sample was heated to 550 ºC in a muffle furnace to cause the volatile solids to be released. The sample was again cooled, and the remaining residue represents the fixed solids portion (USEPA, 2001b).

The volatilization of ammonia from any manure management operation can be highly variable depending on total ammonia concentration, temperature, pH, and storage time. Emissions depended on how much of the ammonia-nitrogen in solution remains as volatile ammonia or reacts to form non-volatile ammonium (NH_4^+). High pH and high temperature favor a higher concentration of neutral ammonia and causes greater ammonia emissions (National Research Council, 2003).

4. Results and Discussion

The TKN values of manure, feed and egg samples of manure barn, barn 4 (manure belt) and barn 5 (high rise) are shown in Table 8 and Table 9.

Table 8. TKN values of manure samples from manure barn, barn 4 and barn 5 in unit of % N.

Month	Manure Barn	Barn 4	Barn 5
May-08	2.1 ± 0.3	2.0 ± 0.2	2.0 ± 0.2
Jun-08	2.8 ± 0.2	1.7 ± 0.1	1.7 ± 0.2
Jul-08	1.9 ± 0.3	2.0 ± 0.2	2.0 ± 0.3
Aug-08	1.6 ± 0.2	2.0 ± 0.2	2.0 ± 0.3
Sep-08	2.2 ± 0.1	1.7 ± 0.3	1.9 ± 0.2
Oct-08	1.7 ± 0.1	1.5 ± 0.2	1.4 ± 0.2
Nov-08	1.8 ± 0.2	2.3 ± 0.2	2.2 ± 0.3
Dec-08	1.7 ± 0.2	2.5 ± 0.3	2.0 ± 0.2
Jan-09	1.5 ± 0.1	1.9 ± 0.1	1.6 ± 0.2
Feb-09	1.9 ± 0.2	2.0 ± 0.3	2.0 ± 0.3
Mar-09	2.2 ± 0.2	1.9 ± 0.2	1.6 ± 0.2
Apr-09	2.1 ± 0.3	1.7 ± 0.2	2.1 ± 0.1
May-09	2.1 ± 0.2	1.9 ± 0.2	2.2 ± 0.2
Jun-09	2.1 ± 0.2	1.8 ± 0.2	1.6 ± 0.2
Jul-09	2.1 ± 0.3	1.9 ± 0.2	2.7 ± 0.2
Aug-09	1.9 ± 0.1	1.9 ± 0.1	2.1 ± 0.1
Sep-09	2.2 ± 0.2	1.8 ± 0.2	1.9 ± 0.2
Oct-09	1.9 ± 0.3	1.6 ± 0.2	1.7 ± 0.1
Nov-09	1.8 ± 0.1	2.2 ± 0.3	2.3 ± 0.2
Minimum	1.5 ± 0.1	1.5 ± 0.2	1.4 ± 0.2
Maximum	2.8 ± 0.2	2.5 ± 0.3	2.7 ± 0.2
Mean	2.0	1.6	1.9
SD	0.3	0.3	0.3

The values reported were the average number of four measurements from each month from May 2008 to November 2009 with their standard deviations. The calculated TKN value of manure from manure barn, barn 4 and barn 5 were reported in % N as 2.0% ± 0.3, 1.6% ± 0.3 and 1.9% ± 0.3, respectively. The TKN value for feed from barn 4 and barn 5 were 2.4% ± 0.2 and 2.3% ± 0.2, respectively. The TKN value for eggs from barn 4 and barn 5 were 1.9% ± 0.2 and 2.0% ± 0.1, respectively.

Table 9. TKN values of feed and egg samples of barn 4 and barn 5 in unit of % N.

Month	Egg 4	Egg 5	Feed 4	Feed 5
May-08	2.0 ± 0.1	1.9 ± 0.2	2.5 ± 0.3	2.2 ± 0.2
Jun-08	2.1 ± 0.2	2.0 ± 0.3	2.6 ± 0.3	1.6 ± 0.2
Jul-08	1.9 ± 0.2	1.7 ± 0.2	2.8 ± 0.2	2.2 ± 0.3
Aug-08	2.0 ± 0.1	2.0 ± 0.2	2.7 ± 0.2	2.4 ± 0.2
Sep-08	2.1 ± 0.2	1.9 ± 0.2	2.6 ± 0.1	2.5 ± 0.2
Oct-08	1.9 ± 0.2	2.0 ± 0.2	2.5 ± 0.2	2.4 ± 0.3
Nov-08	2.2 ± 0.3	2.1 ± 0.3	2.4 ± 0.3	2.3 ± 0.2
Dec-08	2.0 ± 0.3	2.0 ± 0.2	2.5 ± 0.2	2.3 ± 0.1
Jan-09	2.0 ± 0.2	2.0 ± 0.2	2.3 ± 0.2	2.3 ± 0.2
Feb-09	2.1 ± 0.3	2.0 ± 0.3	2.4 ± 0.2	2.2 ± 0.1
Mar-09	1.9 ± 0.2	2.0 ± 0.1	2.3 ± 0.3	2.1 ± 0.2
Apr-09	1.9 ± 0.3	1.9 ± 0.2	2.2 ± 0.1	2.1 ± 0.3
May-09	1.9 ± 0.3	1.8 ± 0.3	2.0 ± 0.2	2.0 ± 0.2
Jun-09	1.5 ± 0.3	1.8 ± 0.2	2.1 ± 0.2	2.6 ± 0.3
Jul-09	1.6 ± 0.1	1.9 ± 0.2	1.9 ± 0.2	2.4 ± 0.1
Aug-09	1.7 ± 0.2	2.2 ± 0.3	2.2 ± 0.3	2.5 ± 0.2
Sep-09	2.0 ± 0.3	2.0 ± 0.2	2.5 ± 0.3	2.2 ± 0.2
Oct-09	1.5 ± 0.2	1.9 ± 0.2	2.5 ± 0.2	2.3 ± 0.2
Nov-09	2.1 ± 0.3	2.1 ± 0.3	2.2 ± 0.2	2.2 ± 0.2
Minimum	1.5 ± 0.3	1.7 ± 0.2	2.0 ± 0.2	1.6 ± 0.2
Maximum	2.2 ± 0.3	2.2 ± 0.3	2.8 ± 0.2	2.6 ± 0.3
Mean	1.9	2.0	2.4	2.3
SD	0.2	0.1	0.2	0.2

Manure management in laying hen facilities can greatly influence NH_3 emission. In comparison, the TKN value of barn 4 was less than of barn 5 (21%) because barn 4 had a conveyor belt system to separate the manure from the housing facility while in barn 5, manure was stored in a pit below. The monthly average values of TKN of manure samples are shown in Fig. 19.

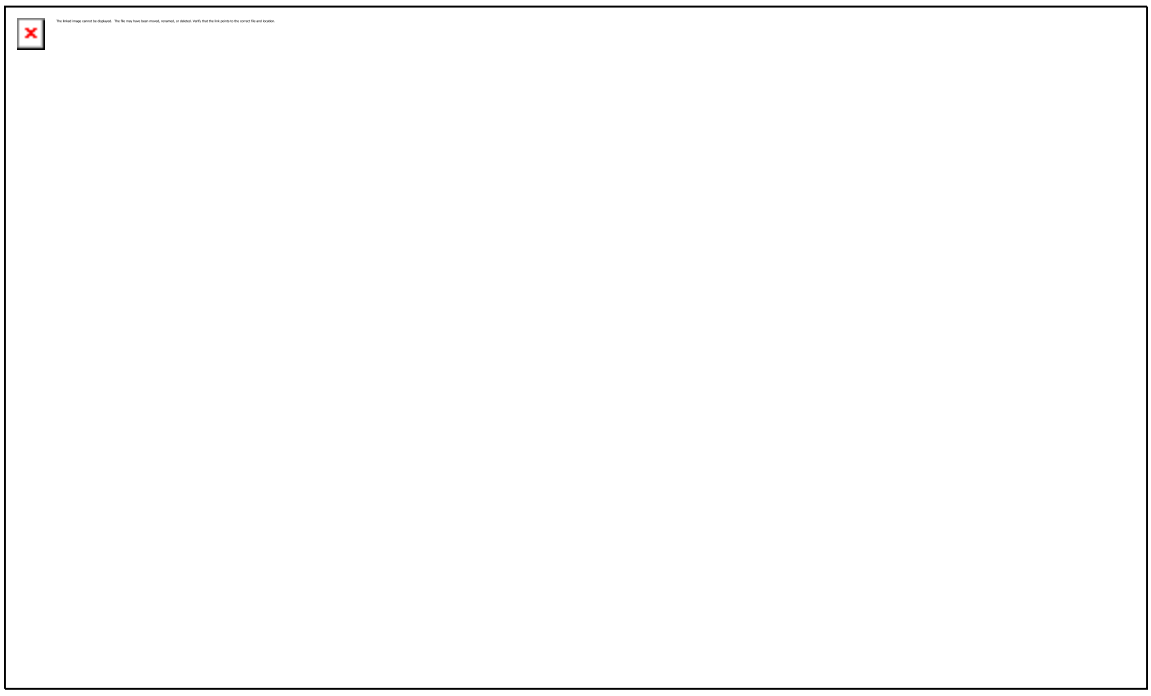

Fig. 19. TKN of manure samples in % N. The standard deviation of the 4 samples collected each month is also shown.

These results further confirmed that the conveyor belt system had a major advantage over the deep pit house system in terms of NH_3-N conservation or prevention of NH_3-N emission.

The NH_3 values of manure barn, barn 4 and barn 5 were shown in Table 10. The calculated NH_3 values for manure barn, barn 4 and barn 5 were reported in unit of mg NH_3/g_{manure} as 1.1 ± 0.2, 0.6 ± 0.1 and 0.8 ± 0.1, respectively. The value for barn 4 and barn 5 were highest in the summer months due to the higher temperature and higher pH values.

Table 10. Ammonia (NH_3) content of manure samples in unit of mg NH_3/g_{manure}

Month	Manure Barn	Barn 4	Barn 5
May-08	1.6 ± 0.2	0.4 ± 0.1	0.9 ± 0.2
Jun-08	1.4 ± 0.1	0.4 ± 0.1	0.8 ± 0.1
Jul-08	1.4 ± 0.2	0.8 ± 0.1	0.6 ± 0.1
Aug-08	1.1 ± 0.1	0.8 ± 0.1	0.7 ± 0.1
Sep-08	1.3 ± 0.1	0.8 ± 0.1	0.7 ± 0.1
Oct-08	0.6 ± 0.1	0.4 ± 0.1	0.6 ± 0.1
Nov-08	0.9 ± 0.1	0.6 ± 0.1	0.8 ± 0.1
Dec-08	0.8 ± 0.1	0.5 ± 0.1	0.5 ± 0.1
Jan-09	0.5 ± 0.1	0.6 ± 0.1	0.7 ± 0.1
Feb-09	1.1 ± 0.1	0.7 ± 0.2	0.4 ± 0.1
Mar-09	1.4 ± 0.1	0.7 ± 0.1	0.6 ± 0.1
Apr-09	1.5 ± 0.2	0.6 ± 0.2	0.9 ± 0.2
May-09	1.1 ± 0.1	0.6 ± 0.1	1.0 ± 0.1
Jun-09	0.8 ± 0.1	0.5 ± 0.1	0.8 ± 0.1
Jul-09	1.1 ± 0.1	0.6 ± 0.1	0.7 ± 0.1
Aug-09	1.2 ± 0.1	0.8 ± 0.1	0.8 ± 0.1
Sep-09	1.1 ± 0.1	0.8 ± 0.2	0.7 ± 0.1
Oct-09	0.8 ± 0.1	0.5 ± 0.1	0.7 ± 0.1
Nov-09	1.0 ± 0.1	0.6 ± 0.1	0.8 ± 0.1
Minimum	0.5 ± 0.1	0.4 ± 0.1	0.4 ± 0.1
Maximum	1.6 ± 0.2	0.8 ± 0.1	1.0 ± 0.1
Mean	1.1	0.6	0.8
SD	0.2	0.1	0.1

The pH values are shown in Table 11. The pH of manures handled as solids can be in the range of 7.5 to 8.5, which results in fairly rapid ammonia volatilization (Susan and Katharine, 2005). Higher temperature in the summer months favors the volatility of NH_3 to ammonia gas which was less soluble in water than NH_4^+. In addition, emissions decreased immediately after belt cleaning. For example in barn 4, the result showed that emissions dropped dramatically from 0.78 mg NH_3/g_{manure} to 0.43 mg NH_3/g_{manure} which

was a reduction of 45% when the barn was cleaned out in October. In barn 5, the result dropped from 0.71 mg NH_3/g_{manure} to 0.60 mg NH_3/g_{manure}, which was a reduction of 16% due to barn cleaning operations.

Table 11. pH values of manure barn, barn 4 and barn 5.

Month	Manure Barn	Barn 4	Barn 5
May-08	8.31 ± 0.02	8.17 ± 0.01	8.25 ± 0.01
Jun-08	8.85 ± 0.02	8.08 ± 0.01	8.45 ± 0.01
Jul-08	8.37 ± 0.01	7.64 ± 0.01	7.32 ± 0.01
Aug-08	8.38 ± 0.01	8.39 ± 0.01	8.44 ± 0.01
Sep-08	8.59 ± 0.01	8.25 ± 0.01	8.16 ± 0.01
Oct-08	8.18 ± 0.01	8.32 ± 0.01	8.22 ± 0.01
Nov-08	8.66 ± 0.01	8.15 ± 0.01	8.43 ± 0.01
Dec-08	8.04 ± 0.01	7.83 ± 0.01	7.74 ± 0.01
Jan-09	8.45 ± 0.02	7.60 ± 0.01	8.32 ± 0.01
Feb-09	8.27 ± 0.01	7.80 ± 0.01	8.39 ± 0.01
Mar-09	8.51 ± 0.02	8.01 ± 0.02	8.28 ± 0.01
Apr-09	8.57 ± 0.02	7.89 ± 0.01	8.27 ± 0.01
May-09	8.41 ± 0.01	7.76 ± 0.01	8.26 ± 0.01
Jun-09	8.40 ± 0.01	8.02 ± 0.01	8.20 ± 0.01
Jul-09	8.30 ± 0.01	7.82 ± 0.01	7.90 ± 0.01
Aug-09	8.21 ± 0.01	8.23 ± 0.01	8.22 ± 0.01
Sep-09	8.35 ± 0.01	8.13 ± 0.01	8.02 ± 0.01
Oct-09	8.08 ± 0.02	8.32 ± 0.01	8.05 ± 0.01
Nov-09	8.46 ± 0.03	8.34 ± 0.01	8.25 ± 0.01
Minimum	8.04 ± 0.01	7.60 ± 0.01	7.32 ± 0.01
Maximum	8.85 ± 0.02	8.39 ± 0.01	8.45 ± 0.01
Mean	8.39	8.04	8.17
SD	0.20	0.25	0.27

The barns were scheduled to be emptied out twice a year, in May and October. These findings indicate that a frequent scraping of manure belt could reduce NH_3

emissions in the ventilated belt house. Fig. 20 shows the monthly average values of NH_3 content of barn 4 and barn 5.

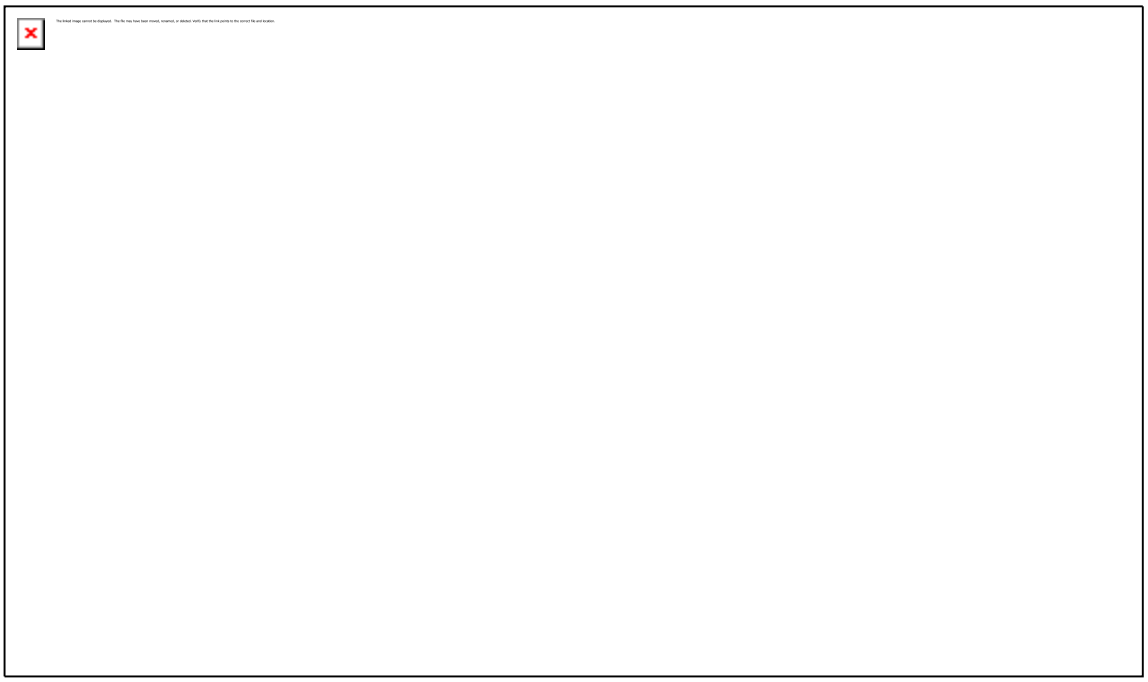

Fig. 20. Ammonia content of manure samples. The standard deviation of the 4 samples collected each month is also shown.

Ammonia emission rates varied seasonally and diurnally. Ammonia emission rates were found to be higher during the late spring and summer than during the rest of the year. Further analysis of the data indicated that emission rates were higher during the warm weather due to higher ventilation rates and were consistent with earlier studies (Liang et al., 2003). According to Ogunlaja (Ogunlaja, 2008), the ventilation rate results from barn 4 ranged from 2.11 $m^3h^{-1}bird^{-1}$ to 3.02 $m^3h^{-1}bird^{-1}$ with an average of 2.74 $m^3h^{-1}bird^{-1}$. Barn 5 building ventilation rates ranged from 1.40 $m^3h^{-1}bird^{-1}$ to 2.34 $m^3h^{-1}bird^{-1}$, with an average of 2.09 $m^3h^{-1}bird^{-1}$. It was observed from the collected data that the inside barn NH_3 concentrations were higher during the early hours of the morning when

most of the fans were not running. But as the day goes by, approaching noon (higher temperature) and for most part of the afternoon, the inside barn concentration is reduced due to a higher number of fans running, thus leading to higher NH_3 emission (Ogunlaja, 2008).

As mentioned previously, little work has been done to date in the US to determine ammonia emission factors. In a review of ammonia emission factors (Faulkner et al., 2008), some recommended factors were provided for the U.S agriculture system. For dry manure handling systems an emission factor of 0.19 kg NH_3/bird-year or 520 mg NH_3/bird-day was given. For wet manure handling systems, 0.11 kg NH_3/bird-year or 300 mg NH_3/bird-day was given. These values were similar to the results obtained in the current study. The average values obtained in this study for barn 4 was 440 ± 180 mg NH_3/bird-day and the average for barn 5 was 540 ± 190 mg NH_3/bird-day.

In work done previously, it was determined that barns which employed the belt system to remove the manure and separate it from the housing tended to have lower emission factors (Fabbri et al., 2007). In the results obtained from this study, the same reduced emissions were observed. The average emission factors for barn 4 was 440 ± 180 mg NH_3/bird-day, which was 99 mg NH_3/bird-day (18%) less than the emission factors of barn 5 of 540 ± 190 mg NH_3/bird-day.

In European studies, the emission factors for barns which employed a manure belt system were generally around 95-170 mg NH_3/bird-day, and barns which contained manure pits were around 380-420 mg NH_3/bird-day. The average factor obtained for the belt system in this research was 440 ± 180 mg NH_3/bird-day, which was about 270 mg NH_3/bird-day higher than the European studies (440 – 170 = 270). The average factor

obtained for the manure pits in this research was 540 ± 190 mg NH_3/bird-day, which was about 120 mg NH_3/bird-day higher than the values in European studies (540 – 420 = 120). Wheeler et al. (2006) stated that lower reported emission rates from broiler houses in Europe were possibly due to the following management practices that differ from those employed in the U.S.: 1) litter was usually changed between each flock, and 2) birds were slaughtered at a lower weight. In this study, the NH_3 emission factors reduction using the ventilated belt technique compared to the deep-pit house technique was 21%.

According to Table 10, the average pH value for manure barn was 8.39 ± 0.20, which was higher than the pH of barn 4 and barn 5, which were 8.04 ± 0.25 and 8.17 ± 0.27, respectively. This would suggest that the manure samples in manure barn would have a higher level of ammonia content (vs. NH_4^+) compared to barn 4 and barn 5. Using the TKN method, the yearly average from May 2008 to November 2009 ammonia content of manure sample was calculated as 1.1 ± 0.2 mg NH_3/g_{manure}, which was higher than of barn 4 (0.62 ± 0.1 mg NH_3/g_{manure}) and barn 5 (0.73 ± 0.1 mg NH_3/g_{manure}). The ammonia in the ambient air of the manure barn was measured at several times during this study (during October (day 14th and 21^{h}) 2008 at sampling site 1 and 2, December (day 2nd and 23rd) 2008 at sampling 1 and 4, May (day 12th and 19th) 2009 at sampling site 2 and 3, and September (day 8th and 15th) 2009) at sampling site 1 and 3 using impinger and IC methods (see Fig. 2, Chapter 2 for the sampling site locations).

The sampling period was two hours for each impinger sampler. The average value for the eight samples was 13.7 ± 3.0 ppm. This value was also higher than the average ammonia concentrations observed in air of barn 4 (11.9 ± 2.9 ppm) and barn 5 (12.7 ± 3.1 ppm). There was less urine in the manure barn, thus the reaction to create ammonia

should be much slower when compared to barn 5. However, the sample measurements showed that the ammonia in the manure barn air was higher than of barn 4 and barn 5. This was believed to be due to lower ventilation rates of the manure barn.

There were only three out of nine fans were running during the sampling periods. The lower ventilation rate of manure belt barn was believed to cause a higher in concentration of ammonia in air within the barn. The calculated nitrogen emission factors of barn 4 and barn 5 are shown in Table 12 and 13, respectively. A plot of monthly ammonia emission from barn 4 and barn 5 was shown in Fig. 21.

The average NH_3 emission of barn 4 was 440 ± 180 mg NH_3/bird-day and of barn 5 was 540 ± 190 mg NH_3/bird-day. The highest NH_3 emission of barn 4 occurred during the month of October-08 as the value of 790 mg NH_3/bird-day while in barn 5, the value was 914 mg NH_3/bird-day and this value occurred during the month of March-09. In addition, during the warm months, from June to August, the emission of barn 4 and barn 5 were both lower than the values in the cold months. Observations showed that the higher values of the TKN and NH_3 during the warm months caused lower values of nitrogen emission.

The percentage of nitrogen loss to the atmosphere was calculated as the ratio of nitrogen emission to the total input nitrogen (in this study, total nitrogen input was NF feed) and time by 100%. The percentage of nitrogen loss per bird to the atmosphere is 16% for barn 4 and 20% for barn 5.

These losses were due to the volatility of uric acid in the chicken urine, the time which the manure was collected and how old the age of the chicken feces, which depended on the storage time.

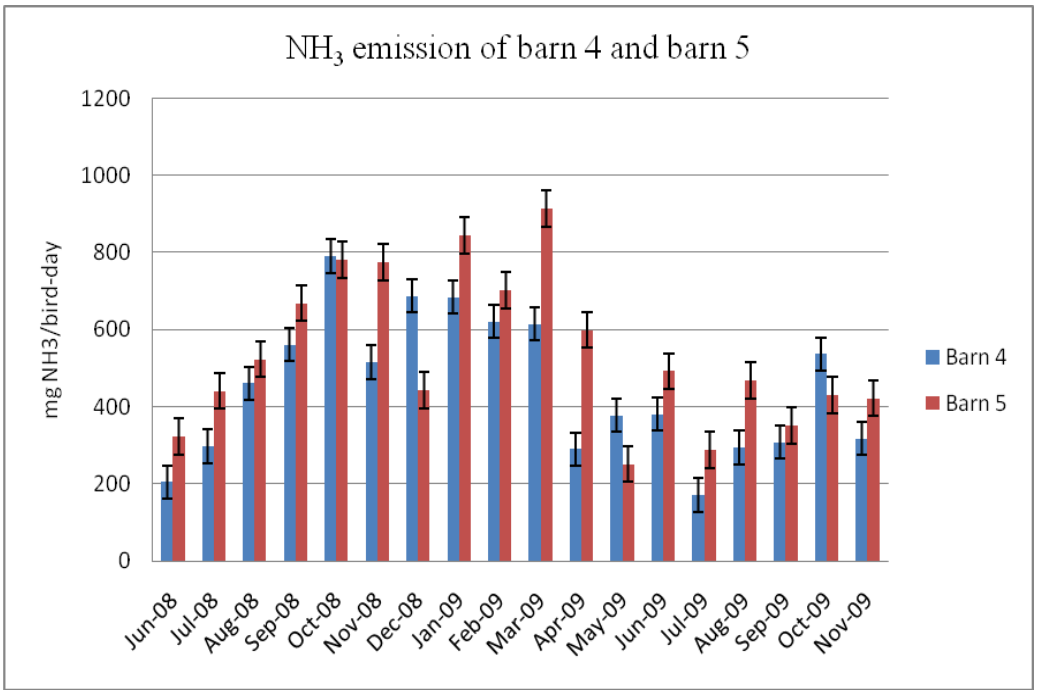

Fig. 21. Ammonia emission of barn 4 and barn 5 in units of mg NH_3/bird-day. The standard deviation of the 4 samples collected each month is also shown.

In general, the NH_3 emission from barn 4 was less than from barn 5. The difference in the yearly average values between the two barns was 123 mg NH_3/bird-day which was equivalent to 13% in reducing the NH_3 emission.

The solid content of manure, feed and egg samples also play an important factor in the determined NH_3 emission levels. Higher moisture content of the manure results in a higher ratio of NH_3/TKN_{manure} stored in the manure that results in a higher percentage of N loss. The results indicated that the quicker the manure dried, the less NH_3 was emitted. Table 14 shows the total solid and volatile solid content of manure samples.

Table 12. Nitrogen emission of barn 4 in unit of mg NH_3/bird-day (NF = Nitrogen flux, EM = emission).

Month	NF feed	NF egg	NF manure	EM NH_3	% N loss
May-08	2200 ± 230	870 ± 110	1100 ± 110	260 ± 22	10
Jun-08	1100 ± 310	110 ± 19	790 ± 78	210 ± 29	16
Jul-08	1900 ± 230	570 ± 76	1100 ± 110	300 ± 37	13
Aug-08	2600 ± 230	880 ± 110	1400 ± 130	460 ± 31	14
Sep-08	2700 ± 250	1100 ± 98	1200 ± 140	560 ± 27	17
Oct-08	2500 ± 230	980 ± 83	890 ± 110	790 ± 32	26
Nov-08	2400 ± 190	1100 ± 78	1100 ± 99	510 ± 26	14
Dec-08	2600 ± 210	890 ± 39	1100 ± 110	690 ± 54	26
Jan-09	2400 ± 240	880 ± 61	940 ± 89	690 ± 39	23
Feb-09	2300 ± 170	760 ± 53	1100 ± 110	620 ± 62	22
Mar-09	2500 ± 210	1100 ± 110	940 ± 97	610 ± 59	20
Apr-09	2200 ± 240	740 ± 29	1200 ± 120	290 ± 35	11
May-09	2300 ± 310	620 ± 31	1400 ± 150	380 ± 58	13
Jun-09	1700 ± 270	46 ± 11	1400 ± 150	380 ± 29	18
Jul-09	1600 ± 230	310 ± 21	1200 ± 130	170 ± 37	9
Aug-09	2200 ± 180	7550 ± 120	1200 ± 110	290 ± 31	11
Sep-09	2500 ± 340	1100 ± 120	1100 ± 86	310 ± 42	12
Oct-09	2600 ± 310	1100 ± 130	1100 ± 70	540 ± 87	20
Nov-09	2500 ± 220	1300 ± 110	980 ± 84	320 ± 45	12
Minimum	1100 ± 310	46 ± 11	790 ± 78	170 ± 37	9
Maximum	2700 ± 250	1300 ± 110	1400 ± 130	790 ± 32	26
Mean	2200	790	1100	440	16
SD	420	330	160	180	5

Table 15 and 16 show the total solid and volatile solid content of feed and egg samples. The results showed that the less volatile solid that the sample contained, the lower the TKN and NH_3 values. The yearly average volatile solid content of manure samples (in %) for barn 4 and barn 5 were 21.9 ± 1.3% and 22.5 ± 1.8%, respectively.

The yearly average volatile solid of egg samples for barn 4 and barn 5 were 20.1 ± 1.4% and 21.6 ± 1.9%, respectively. The yearly average volatile solid of feed samples for barn 4 and barn 5 were 64.7 ± 3.5% and 63.9 ±3.2%, respectively.

Table 13. Nitrogen emission of barn 5 in unit of mg NH_3/bird-day (NF = Nitrogen flux, EM = emission).

Month	NF feed	NF egg	NF manure	EM NH_3	% N loss
May-08	ND	ND	ND	ND	ND
Jun-08	1700 ± 150	310 ± 66	1100 ± 120	320 ± 39	16
Jul-08	1300 ± 210	120 ± 26	790 ± 110	440 ± 32	28
Aug-08	2300 ± 170	910 ± 89	990 ± 99	520 ± 28	18
Sep-08	2700 ± 150	1100 ± 110	1100 ± 110	670 ± 110	20
Oct-08	2600 ± 220	1100 ± 150	910 ± 120	780 ± 230	24
Nov-08	2700 ± 310	1200 ± 71	930 ± 87	770 ± 120	23
Dec-08	2600 ± 160	1100 ± 27	1300 ± 93	440 ± 96	9
Jan-09	2500 ± 130	1100 ± 67	790 ± 82	840 ± 210	27
Feb-09	2400 ± 190	1100 ± 79	750 ± 130	710 ± 99	24
Mar-09	2300 ± 250	770 ± 39	760 ± 98	910 ± 110	32
Apr-09	2200 ± 240	1100 ± 99	740 ± 94	590 ± 95	21
May-09	1800 ± 230	640 ± 120	930 ± 180	260 ± 26	11
Jun-09	1900 ± 130	340 ± 93	1200 ± 230	490 ± 89	20
Jul-09	2200 ± 210	810 ± 150	1100 ± 290	290 ± 39	11
Aug-09	2300 ± 330	880 ± 230	1100 ± 110	470 ± 99	16
Sep-09	2400 ± 360	1100 ± 180	990 ± 48	350 ± 58	14
Oct-09	2600 ± 290	1200 ± 210	990 ± 43	430 ± 94	16
Nov-09	2700 ± 230	1300 ±310	990 ± 28	420 ± 91	15
Minimum	1300 ± 210	120 ± 26	740 ± 94	260 ± 26	9
Maximum	2700 ± 230	1300 ±310	1300 ± 93	910 ± 110	32
Mean	2300	890	970	540	20
SD	410	340	160	190	6

ND: not determined.

Table 14. Total solid and volatile solid of manure samples.

Month	Barn 4		Barn 5	
	%TS	%VS	%TS	%VS
May-08	35.4 ± 1.7	20.4 ± 1.4	33.6 ± 2.1	19.2 ± 1.1
Jun-08	40.9 ± 2.1	20.0 ± 0.8	36.3 ± 1.6	20.6 ± 0.7
Jul-08	40.1 ± 1.6	23.0 ± 1.2	35.1 ± 1.1	22.4 ± 0.8
Aug-08	38.8 ± 1.6	25.0 ± 1.5	42.0 ± 1.7	25.5 ± 1.2
Sep-08	34.0 ± 1.4	22.6 ± 1.1	40.8 ± 1.8	26.2 ± 1.6
Oct-08	37.0 ± 1.6	21.2 ± 1.6	36.0 ± 1.9	23.5 ± 0.9
Nov-08	41.6 ± 1.8	22.4 ± 1.1	36.6 ± 2.1	22.2 ± 1.4
Dec-08	35.7 ± 1.9	23.1 ± 1.7	35.2 ± 2.3	23.2 ± 1.6
Jan-09	41.6 ± 2.2	24.4 ± 2.0	36.4 ± 2.1	22.7 ± 2.1
Feb-09	39.5 ± 1.4	21.4 ± 1.8	38.3 ± 1.5	22.4 ± 1.3
Mar-09	37.7 ± 1.1	21.5 ± 0.7	35.7 ± 2.1	21.9 ± 2.3
Apr-09	36.0 ± 1.5	21.2 ± 1.4	32.8 ± 1.7	20.4 ± 1.2
May-09	35.1 ± 1.8	20.7 ± 1.2	34.2 ± 1.1	20.5 ± 1.6
Jun-09	39.2 ± 1.7	21.0 ± 1.1	34.7 ± 1.4	19.5 ± 1.7
Jul-09	41.0 ± 2.0	21.3 ± 1.6	34.7 ± 1.0	22.6 ± 1.5
Aug-09	39.0 ± 2.4	21.3 ± 1.4	40.2 ± 1.6	23.1 ± 1.9
Sep-09	35.0 ± 1.4	23.0 ± 1.8	38.6 ± 1.8	22.8 ± 1.5
Oct-09	37.0 ± 1.9	21.7 ± 1.2	36.8 ± 2.0	23.6 ± 1.3
Nov-09	40.5 ± 2.5	21.2 ± 1.3	37.6 ± 1.9	23.4 ± 1.2
Minimum	34.0 ± 1.4	20.0 ± 0.8	32.8 ± 1.7	19.2 ± 1.1
Maximum	41.6 ± 2.2	25.0 ± 1.5	42.0 ± 1.7	26.2 ± 1.6
Mean	38.2	21.9	36.6	22.5
SD	2.5	1.3	2.3	1.80

TS: total solid, VS: volatile solid.

Table 15. Total solid and volatile solid of feed samples (%).

Month	Feed 4		Feed 5	
	%TS[a]	%VS[b]	%TS[a]	%VS[b]
May-08	87.5 ± 1.8	57.7 ± 1.3	87.2 ± 2.1	51.2 ± 1.5
Jun-08	88.3 ± 2.3	55.1 ± 1.5	88.6 ± 1.3	53.2 ± 2.0
Jul-08	86.9 ± 2.5	62.7 ± 1.7	86.9 ± 1.6	58.9 ± 1.5
Aug-08	88.8 ± 1.6	73.4 ± 1.4	87.8 ± 1.4	68.7 ± 1.7
Sep-08	88.0 ± 1.7	71.9 ± 1.8	88.2 ± 1.7	70.2 ± 1.3
Oct-08	87.7 ± 1.0	66.7 ± 2.1	82.8 ± 1.5	65.9 ± 1.8
Nov-08	88.7 ± 1.4	63.4 ± 2.7	84.5 ± 1.4	63.7 ± 2.1
Dec-08	88.8 ± 1.6	63.5 ± 1.8	86.4 ± 1.8	65.9 ± 1.0
Jan-09	86.8 ± 1.9	63.0 ± 1.9	86.6 ± 1.1	66.0 ± 1.5
Feb-09	87.2 ± 2.1	63.0 ± 2.3	84.7 ± 1.6	58.7 ± 1.6
Mar-09	85.2 ± 1.4	62.4 ± 2.4	86.1 ± 1.4	67.4 ± 1.4
Apr-09	86.4 ± 1.5	65.2 ± 1.5	87.7 ± 1.0	65.3 ± 1.3
May-09	87.3 ± 1.6	62.3 ± 1.3	88.5 ± 1.6	61.4 ± 1.7
Jun-09	87.3 ± 1.7	61.9 ± 2.1	89.4 ± 1.8	69.1 ± 2.1
Jul-09	89.9 ± 1.3	63.6 ± 1.5	85.2 ± 2.0	62.3 ± 1.1
Aug-09	85.7 ± 2.3	70.1 ± 1.8	85.3 ± 1.2	66.3 ± 1.8
Sep-09	89.0 ± 2.1	69.6 ± 1.4	87.5 ± 1.5	68.3 ± 1.2
Oct-09	88.8 ± 1.6	67.4 ± 1.4	84.3 ± 1.3	66.7 ± 1.4
Nov-09	87.2 ±1.8	65.5 ± 1.3	85.3 ± 1.7	65.4 ± 1.2
Minimum	85.2 ± 1.4	55.1 ± 1.5	82.8 ± 1.5	51.2 ± 1.5
Maximum	89.9 ± 1.3	73.4 ± 1.4	89.4 ± 1.8	70.2 ± 1.3
Mean	87.7	64.7	86.5	63.9
SD	1.2	3.5	1.8	3.2

[a]TS: total solid, [b]VS: volatile solid.

Table 16. Total solid and volatile solid of egg samples (%).

Month	Egg 4		Egg 5	
	%TS[a]	%VS[b]	%TS[a]	%VS[b]
May-08	20.3 ± 1.3	17.3 ± 1.0	19.6 ± 1.2	16.8 ± 1.3
Jun-08	20.5 ± 0.9	18.2 ± 1.3	24.3 ± 1.3	22.1 ± 1.5
Jul-08	20.2 ± 1.2	17.5 ± 1.5	20.6 ± 1.5	19.66 ± 0.7
Aug-08	22.1 ± 1.5	20.1 ± 1.9	22.5 ± 1.1	21.5 ± 1.1
Sep-08	22.8 ± 1.9	20.7 ± 1.4	23.2 ± 1.4	22.0 ± 1.0
Oct-08	22.2 ± 1.3	20.7 ± 1.6	24.0 ± 1.8	21.2 ± 1.4
Nov-08	20.0 ± 1.5	19.1 ± 1.8	26.3 ± 1.0	24.8 ± 1.1
Dec-08	21.3 ± 1.7	20.2 ± 1.5	23.3 ± 0.8	21.0 ± 1.0
Jan-09	24.1 ± 1.8	22.7 ± 1.4	25.2 ± 1.2	24.1 ± 1.0
Feb-09	23.1 ± 1.3	21.2 ± 1.7	25.0 ± 1.4	23.2 ± 1.3
Mar-09	22.9 ± 1.5	21.2 ± 1.5	26.6 ± 1.5	24.5 ± 1.1
Apr-09	21.0 ± 1.2	19.9 ± 1.3	24.2 ± 1.2	22.5 ± 1.8
May-09	21.1 ± 1.1	18.7 ± 1.4	21.9 ± 1.6	18.8 ± 1.5
Jun-09	21.8 ± 1.7	19.5 ± 1.3	23.1 ± 1.4	22.0 ± 1.4
Jul-09	22.0 ± 2.1	20.8 ± 1.7	21.2 ± 1.2	20.1 ± 1.6
Aug-09	23.1 ± 1.3	21.4 ± 1.5	23.9 ± 1.4	22.0 ± 1.7
Sep-09	21.9 ± 2.0	21.0 ± 1.2	22.7 ± 1.3	19.8 ± 1.9
Oct-09	23.2 ± 1.4	21.3 ± 1.1	23.7 ± 1.5	21.5 ± 1.3
Nov-09	21.2 ± 1.7	19.6 ± 1.5	24.8 ± 1.6	22.1 ± 1.3
Minimum	20.0 ± 1.5	17.3 ± 1.0	19.6 ± 1.2	16.8 ± 1.3
Maximum	24.1 ± 1.8	22.7 ± 1.4	26.6 ± 1.5	24.1 ± 1.0
Mean	21.9	20.1	23.5	21.6
SD	1.2	1.4	1.8	1.9

[a]TS: total solid, [b]VS: volatile solid

5. Conclusions

Using the TKN method, chicken manure, feed and eggs were sampled and analyzed to determine their percentage nitrogen. The obtained results revealed the fact that drying and removing the manure by means of manure belt system reduced emissions. These values were comparable to values from previous studies in Europe. Using the TKN method, the calculated ammonia emission factors in this study were 440 ± 180 mg NH_3/bird-day for barn 4 (manure belt) and 540 ± 190 mg NH_3/bird-day for barn 5 (high rise). Comparison of the TKN method with the emission factors studies in Europe, the emission factors in U.S. are higher than in Europe. This is believed to be due to the differences in housing facilities, manure management practices, climate, etc. between the U.S and Europe. In the future studies, the U.S. should apply strategies to reduce ammonia emissions. These strategies include application of urease inhibitors (e.g. N-n-butyl thiophosphoric triamide, cyclohexylphosphoric triamide, and phenyl phosphorodiamidate), separation of feces and urine in order to prevent hydrolysis of urea by using the conveyor belt, manipulating dietary (this is accomplished through the addition of acidogenic phosphorus sources and/or calcium salts to feed in order to counteract the pH increases that occur as a result of urea hydrolysis), etc. (National Research Council, 2003; Kurvits and Marta, 1998).

CHAPTER 4

SUMMARY AND CONCLUSION

The National Air Emission Monitoring Study (NAEMS) project was funded by the Agricultural Air Research Council (AARC) to evaluate agricultural emissions nationwide. Utah State University (USU) is conducting a parallel study on agricultural emissions at a Cache valley poultry facility. As part of this parallel study, samples of animal feed, eggs and animal waste were collected weekly from three poultry housing and manure storage barns (designated: manure barn, barn 4 - manure belt and barn 5 - high rise) from May 2008 to November 2009. These samples were analyzed to determine the ammonia emission and total nitrogen content of animal production and animal waste at the Cache Valley poultry facility. Using the total Kjeldahl nitrogen method, the ammonia content and total Kjeldahl nitrogen content of animal production and waste in a poultry facility have been successfully analyzed. The volatilization of ammonia from any manure management operation can be highly variable depending on total ammonia concentration, temperature, pH, and storage time. Ammonia emissions were observed to not be constant over the year, but change with the seasons. The results show that the value of ammonia emissions were higher in the summer months as compared to the colder months of the year, presumably due to the increasing volatility of ammonia with increasing temperature. To predict the upper limit of ammonia emission, the nitrogen balance for the animal production system was determined using a mass balance approach. The mass balance-based method calculates emission or nitrogen loss to the environment by the difference between all inputs (N_{input}) and measurable outputs (N_{output}) for the

system under study. N_{input} is based upon the animal feed. N_{output} includes animal produced eggs and manure. The obtained results revealed the fact that drying and removing the manure by means of manure belt system reduced emissions.

The ammonia and volatile organic amine emissions in ambient air at a Cache Valley poultry facility were sampled using an acidified-sulfuric acid trap solution in an impinger train with ion chromatography (IC) detection. The air was sampled at barn 4 (manure belt), barn 5 (high rise) and the manure barn. IC method was developed to perform separations with a gradient program (various compositions of 10 mM MSA and deionized water as eluent) instead of isocratic separations. The results showed that ammonia concentrations in ambient air can be successfully quantified using impinger based air sample collection and ion chromatography separation. However, no organic amines were detected in any of the collected ambient air samples using the same method. Comparison of the results from the impinger/ion chromatography method with results obtained at the same site using a photo acoustic field gas monitor in another study showed that the two methods measured similar ammonia concentrations in the ambient air.

Because there were no organic amines detected by the IC method, another study was conducted to determine if the organic amines are not being observed because they have too low a vapor pressure to be sampled efficiently by the impinger or if they are trapped as salts within the manure, or are of too low a concentration to be observed by the IC method. Alternately, they may simply not be present in the sample. Limits of detection of organic amines in air were studied. The results showed that the organic amines in the manure must occur at a minimum concentration of 1 ppm in order to have sufficient

vapor pressure so that enough is transported to the impingers for trapping and subsequently be detected by the IC.

Because previous measurements indicated that a poultry facility maybe the single biggest source of ammonia in Cache Valley and that organic amines have been observed at other animal farming operations (swine and cow), it was hypothesized that organic amines might be emitted at the poultry farm under study in addition to ammonia. However, no organic amines from the poultry facility were ever detected in the samples collected by the ion chromatography with the trapping impingers methods employed in these studies. Thus, the hypothesis of significant concentrations of organic amines being present in ambient air in the various barns is invalid. Further studies to determine if any organic amines are tide-up within the manure as non-volatile species (chemisorbed or physisorbed to the manure) will require an alternate analysis on sample method. One approach to answering this question might involve using solvent extraction of the manure samples, followed by ion chromatography.

No organic amines were detected in this study using the impinger/ion chromatography method. However, earlier published studies (Schiffman et al., 2001; Devos et al., 1990; Filipy et al., 2006) had detected methylamine, trimethylamine and triethylamine in low ppb concentrations in dairy and swine facilities by using Tenax trapping tubes and GC/MS detection. Table 17 shows a comparison of the impinger/IC method's detection limits and the organic amine concentrations detected in the previous studies. The fact that organic amines were detected in dairy and swine facilities, but were not detected at the poultry facility being studied, may be due to differences in cow and

swine feed compared to the laying hens feed. Alternately, it may be due to differences in the animal's metabolism that causes differences in the manure composition.

Table 17. IC detection limits compared with the concentrations of organic amines detected in alternate studies at dairy and swine farms.

Analyte	IC LOD (ppb in air)	Previous studies in dairy and swine farms (ppb in air)	References
Methylamine	108	18-24	Schiffman et al., 2001; Devos et al., 1990
Trimethylamine	27	24	Schiffman et al., 2001; Filipy et al., 2006
Triethylamine	10	309	Schiffman et al., 2001

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APPENDIXES

Appendix A: Calculation volume of individual amine compound in the original air sample:

Date: August 10, 2009

Location: barn 5

Sample: impingers

$V_a = (N)(0.1)(24.04)(0.001)/(FW_a)$

Where:

V_a = Volume of individual amine gas in the sample of gas taken from the source

N = Average concentration of amine (mg/L) in the solutions obtained from the two impinger ((Impinger 1 concentration + Impinger 2 concentration)/2)

0.10 = Conversion factor, assuming sample in each of the two impingers was diluted to 50 mL (0.10 L)

24.04 = Liters of ideal gas per mole of substance

0.001 = Factor to convert mg/L to g/L

FW_a = Formula weight of amine analyte

FW of Ammonia (NH_3): 17.0 g/mol

From the IC chromatograms, the concentrations of the first and the second impinger were calculated based on peak areas and conductivity.

N_1 = 27.2 ppm (mg/L) and N_2 = 5.4 ppm (mg/L)

N = (27.2 ppm + 5.4 ppm)/2 = 16.3 ppm

V_a = (16.3 mg/L x 0.1 x 24.04 L/mole x 0.001 g/L)/17.1 g/mole = 0.00231 L

Appendix B: The volume of gas sample was corrected to the standard conditions:

Date: August 10, 2009

Location: barn 5

Sample: impingers

$V_{m(std)} = V_m(T_{std}/T_m)[(P_{bar} + \Delta H/13.6)/P_{std}]$

Where:

$V_{m(std)}$ = Volume of gas sample, corrected to standard conditions

V_m = Volume of gas sample

T_{std} = Standard absolute temperature, 293 K

T_m = Absolute average temperature during sampling, K

P_{bar} = Barometric pressure at the sampling site, mm Hg

P_{std} = Standard absolute pressure, 760 mm Hg

ΔH = Impinger pressure change during sampling period, mm of H_2O

13.6 = Specific gravity of mercury

V_m = 194.3 L (1.27 L/min x 153 min = 194 L); T_{std} = 293 K; T_m = 309 K; P_{bar} = 675.0 mm Hg; P_{std} = 760.0 mm Hg; ΔH = 141 mm H_2O

$V_{m(std)}$ = 194.3 L x (293 K/309 K) x [(675.0 mmHg + 141/13.6)/760.0 mm Hg]

$V_{m(std)}$ = 166 L

Thus, the concentrations C_a (reported in ppm) of ammonia present in the gas sample was calculated:

$C_a = V_a/V_{m(std)} \times 10^6$

$C_a = 0.00231 \text{ L}/166 \text{ L} \times 10^6$

$C_a = 13.9$ ppm

The original concentration of ammonia present in the air after the recovery correction (recovery of ammonia is 88.6%):

$13.9 \times 100/88.6 = 15.7$ ppm

Appendix C: Calculation of detection limit of organic amines in air:

Analyte: methylamine

FW: 31.06 g/mol

$V_a = (N)(0.1)(24.04)(0.001)/(FW_a)$

V_a = (0.171 mg/L x 0.1 x 24.04 L/mole x 0.001 g/L)/31.06 g/mole = 0.0000131 L

$V_{m(std)} = V_m(T_{std}/T_m)[(P_{bar} + \Delta H/13.6)/P_{std}]$

V_m = 132 L (1.02 L/min x 129 min = 132 L); T_{std} = 293 K; T_m = 296 K;

P_{bar} = 688.0 mm Hg; P_{std} = 760.0 mm Hg; ΔH = 140 mm H_2O

$V_{m(std)}$ = 132 L x (293 K/296 K) x [(688.0 mm Hg + 140/13.6)/760.0 mm Hg]

$V_{m(std)}$ = 121 L

Detection limit of methylamine in air (ppb):

$C_a = V_a/V_{m(std)} \times 10^6$

C_a = 0.0000131 L/121 L x 10^6

C_a = 0.108 ppm = 108 ppb

Appendix D: Calculation for TKN content in %N

Date: August 10, 2009

Location Barn 4

Sample: Manure

Sample weight (g) = 1.354 g

H_2SO_4 normality = 0.17 N

Titrant (mL) = 10.3 mL

TKN_{manure} = [10.3 mL x 0.17 N x 1.4007*] / 1.354 g

TKN_{manure} = 1.8 % N

*1.4007 is a factor to convert the amount of NH_3-N or TKN to %N:

In this study, dilution factor = 10

(14.007 x 10)/100 = 1.4007

Appendix E: Calculation for NH_3 content in mg NH_3/g_{manure}

Date: August 10, 2009

Location Barn 5

Sample: Manure

Sample weight (g) = 2.245 g

H_2SO_4 normality = 0.17 N

Titrant (mL) = 8.1 mL

$NH_3\text{-}N_{manure}$ = [8.1 mL x 0.172 N x 1.4007] / 2.245 g

$NH_3\text{-}N_{manure}$ = 0.87 mg NH_3/g_{manure}

Appendix F: Calculation for NH_3 emission in mg NH_3/bird-day

Notations and data required for a Nitrogen Balance

Quantity	Unit	Notation
Daily feed consumption rate	kg/barn-day	m'_{feed}
Number of animals	birds/barn	n_b
TKN content of feed	mg/g	R_{Nfeed}
Manure production rate	tons/barn	w_{man}
TKN content of manure	mg/g	$R_{N:man}$
Average egg mass	g	m_{egg}
Production egg efficiency	egg/bird-day	ζ_{egg}
TKN content of egg	mg/g	R_{Negg}

Sample Calculation for Nitrogen Flux

Date: August 10, 2009

Location Barn 4

$R_{Nfeed} =$ 2.4 mg N/g

$m'_{feed} =$ 10466 kg/barn-day

$m'_{feed} =$ 99 g/bird-day

$n_b =$ 105723 birds

$NF_{D:feed} = R_{Nfeed} * m'_{feed}$ (g/bird-day)

$NF_{D:feed}$ = (2.4 mg N/g* 99 g/bird-day) = 240 mg N/bird-day

$R_{Negg} =$ 1.6 mg N/g

$m_{egg} =$ 61 g

$\zeta_{egg} =$ 0.845 egg/bird-day

$NF_{D:egg} = m_{egg} * \zeta_{egg} * R_{Negg}$

$NF_{D:egg}$ = 61 g/egg * 0.845 egg/bird-day * 1.6 mg N/g = 83 mg N/bird-day

$R_{N:man} =$ 1.5 mg N/g

$w_{man} =$ 25 tons/week

$w_{man=}$ 33 g/bird-day

$NF_{man} = R_{N:man} * w_{man}$

NF_{man} = 1.5 mg N/g * 33 g/bird-day = 51 mg N/bird-day

The NH_3 emission in mg/bird-day was calculated as the following:

$EM_{NH3} = (NF_{feed} – NF_{egg} – NF_{man}) \times 1.2143$

where 1.2143 is used to convert molar mass of N to molar mass of NH_3

EM_{NH3} = (240 mg N/bird-day – 83 mg N/bird-day – 51 mg N/bird-day) x 1.2143

EM_{NH3} = 130 mg NH_3/bird-day