DISSERTATION

CHARACTERIZATION AND QUANTIFICATION OF AIR EMISSIONS FROM DAIRIES

Submitted by

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WE HEREBY RECOMMEND THAT THE **DISSERTATION** PREPARED UNDER OUR SUPERVISION BY NICHOLE MARIE MARCILLAC ENTITLED QUANTIFICANTION AND CHARATERIZATION OF AIR EMISSIONS FROM DAIRIES BE ACCETED AS FULLFILLING IN PART REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILIOSOPHY.

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ABSTRACT OF DISSERTATION

CHARACTERIZATION AND QUANTIFICATION OF AIR EMISSIONS FROM DAIRIES

Animal agriculture is a significant and growing source of atmospheric pollutants. The primary pollutants of interest are ammonia (NH_3), ammonium particulates (NH_4^+), carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), volatile organic compounds (VOC), odor, and hydrogen sulfide (H_2S). These species are of interest due to their negative impacts on the environment, air quality, and human health. A reduction of pollutants with best management practices is vital to the sustainability of livestock production. In order to mitigate pollutants from livestock operations, accurate quantification and characterization of the seasonality, spatial variability, and behavior of each species is necessary. The objective of this dissertation was to quantify, characterize, and offer mitigation solutions for air emissions from livestock operations with a focus on dairies and feedlots. First, a comprehensive literature review was conducted on the impacts, emissions values, and measurement techniques of each pollutant. Second, a review of best management practices was compiled to offer solutions to reduce emissions from dairy and feedlot operations. Third, we created a unique measurement system that was able to characterize the vertical and horizontal variability of emissions plumes from dairies using helium balloons and sampling equipment attached to the balloon tether lines. We validated the system with laboratory and field trials and found it to work well under field conditions. Lastly, we used this novel system to quantify and characterize emissions of NH_3, NH_4^+, nitric acid, CO_2, N_2O, and CH_4, from two dairy operations in Colorado. We found that emissions were different from the two operations, and there was strong seasonal, vertical, and horizontal plume variability within each dairy. These results can be used to better characterize emissions from dairy operations and allow researchers, producers, and regulators to better understand and mitigate harmful air emissions, while maintaining agriculture in Colorado.

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Remember, “It ain’t what you don’t know that gets you into trouble. It’s what you know for sure that just ain’t so.” – Mark Twain.

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CHAPTER I

LITERATURE REVIEW

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INTRODUCTION

Animal agriculture has been identified as a major, growing source of atmospheric pollutants in recent years. With the decreasing distance of agriculture from urban and suburban communities, livestock operations are being acknowledged more frequently as sources of odor and as contributors to human health concerns (Shiffman, 1998; Shiffman et al., 1995, 2000). Studies are also noting the impact of livestock emissions on global climate change, vegetation changes, soil acidification, water eutrophication, and natural ecosystem impacts (de Boer, 2003; Krupa, 2003). In Colorado, Rocky Mountain National Park is a prominent example of the impact of nitrogen deposition from ammonia, ammonium particulates, and NOx on fragile mountain ecosystems (Fenn et al., 2003; Baron, 2006). Animal agriculture, in particular dairy operations, has been credited as a significant contributor to those nitrogen emissions, emitting large quantities of ammonia into the atmosphere and contributing to ammonium particulate formation (EPA, 2005). Additionally, cattle have been recognized for years as a significant contributor of methane (IPCC, 2006), a potent greenhouse gas. With cattle numbers on the rise in many states, agriculture's contribution to regional nitrogen deposition and global climate change is ever increasing.

Current estimates predicting emissions from livestock operations are variable due to large variations in management strategies and geographic climate effects. Models have been created to address some of those issues (Quinn et al., 2001; Pinder et al., 2004; Liang et al., 2004; Kebreab et al., 2004), but a comprehensive all-inclusive model is not yet available for both nitrogen and greenhouse gases. Currently, most models don't take seasonality or emission height into consideration, both of which can significantly impact emission estimates (Marcillac et al., 2006). This could be due to the fact that limited emission data exists for estimating pollutants at increased heights (greater than 10 m) and distances downwind of livestock operations, and models don't predict plume height greater than a few meters (Quinn et al., 2001).

The following literature review focuses on the major atmospheric pollutants emitted from animal agricultural operations (ammonia, ammonium, particulate matter, methane, carbon dioxide, and nitrous oxide) and addresses the on-farm sources, environmental and human health impacts of each one. Additionally, a comprehensive look at current emission estimates from dairy operations for each compound is presented along with measurement techniques to quantify those emissions.

MAJOR ATMOSPHERIC POLLUTANTS

Ammonia

Emission Sources

Globally, agriculture is the largest source of atmospheric ammonia, with animal agriculture accounting for approximately 40% of total ammonia emissions (mainly from manure), and crop agriculture contributing an additional 23% from synthetic fertilizer application and crop emissions (Bowman et al., 1997). Ammonia is produced on livestock operations when urea ($(NH_2)_2CO$) in urine combines with the urease enzyme present in feces and soil and rapidly hydrolyzes to form ammonia gas and carbamine acid (NH_2COOH), which decomposes to release ammonia gas and carbon dioxide (1).

$$(NH_2)_2CO + H_2O \text{ (+urease)} \rightarrow NH_2COOH + NH_{3(g)}$$

$$NH_2COOH \rightarrow NH_{3(g)} + CO_{2(g)} \qquad (1)$$

The reaction is quick, taking anywhere from 2 to 10 hours for ammonia volatilization to peak after mixing of urine and feces (Muck, 1981; James et al., 1999). The quantity and rate of ammonia volatilization from manure depends on a variety of factors. The primary factor affecting the amount of ammonia volatilized from manure is the percentage of dietary crude protein (nitrogen) consumed by animals in feed rations. An increase in crude protein in the diet has been shown to exponentially increase manure nitrogen content and subsequent ammonia emissions (Frank et al., 2002; Frank and Swensson, 2002; Cole et al., 2005). This is because the majority of excess dietary nitrogen is excreted in the urine as urea (70%; Misselbrook et al., 2005; Todd et al., 2006), which readily volatilizes as ammonia in the presence of the urease enzyme, which is found in abundance in manure and on almost all farmyard surfaces and soils. Additional factors that influence ammonia volatilization from manure are manure management techniques, pH, temperature, relative humidity, and wind speed (Muck, 1982; Voorburg and Kroodsma, 1992; Beck et al., 2004; Zhang et al., 2005). Since there is such a large and constant supply of manure on livestock operations, there are many opportunities for ammonia volatilization to occur.

Model predictions show that of the ammonia emitted from dairy manure, manure application accounts for the greatest portion of volatilization (42 %), followed by housing (30 %), storage (14 %), and animals grazing pasture (14 %) (Pinder et al., 2004). Additional non-animal sources of ammonia, which contribute to the total global ammonia emission estimate, in order of contribution, include synthetic fertilizers, oceans, biomass burning, crops and crop decomposition, natural soils, and human excreta (Bowman et al., 1997).

Environmental Impact

In the summer months, ammonia concentrations downwind (200 m from source) from a dairy can reach up to 420 ppb during the hottest part of the day near ground level (2m) (Marcillac et al., 2006), which may only represent about 82% of the ammonia concentration at the source (McGinn et al., 2003) under these conditions. Source emissions (i.e barns, drylots, and lagoons) are usually much higher, reaching levels of over 20 ppm in heavily manured areas (Koerkamp et al., 1998). When released into the atmosphere, these high concentrations of ammonia can have detrimental environmental impacts on both natural ecosystems and atmospheric visibility.

When in gaseous form, ammonia has a short atmospheric lifetime of only a few hours (Finlayson-Pitts and Pitts, 2000) and usually deposits near (distance varies based on climatic conditions) its source via wet or dry deposition. Since ammonia gas is highly soluble in water, it readily dissolves in atmospheric water vapor in the lower atmosphere and is deposited back to the Earth's surface via wet deposition (rain). In dry climates or seasons, dry deposition to surrounding plant and soil surfaces is the primary sink for ammonia gas (Finlayson-Pitts and Pitts, 2000). Vegetation can also be a sink for ammonia if the ammonia concentration in the plant is less than the atmospheric concentration around the plant (Moiser, 2001). The net exchange of ammonia depends on several interacting factors, thus a simple description of ammonia exchange between the plant and atmosphere has not been established (Moiser, 2001). However, if plants have a greater ammonia concentration than the atmosphere, rather than diffusing into plant tissues, ammonia will be deposited to plant surfaces contributing to excess nitrogen load, or will be deposited to surrounding soils. When ammonia reaches the soil surface, it usually absorbs to the soil or reacts with water in the soil and is converted into its ionic form, ammonium (NH_4^+). In basic soil at pH 9.2 (NH_4^+ pKa = 9.2), ammonia and ammonium will be present in equal amounts, and ammonia emission will typically be higher. However, at a pH of 7.2 and below, ammonia reacts with hydrogen ions (H^+) present in the soil to form ammonium ion, which at this pH, represents about 99% of the solution while ammonia only represents 1%, dramatically decreasing the ammonia volatilization potential. The ammonium left in the soil eventually disassociates or is nitrified into nitrite (NO_2^-) or nitrate (NO_3^-) by nitrifying bacteria, and releases H^+ into the soil (Nadelhoffer, 2001; de Boer, 2003). If not taken up by biomass, the surplus H^+ eventually leads to formation of an acidic soil environment, and nitrogen loss via ammonia volatilization will not occur due to processes described above. The surplus nitrogen in the soil will either be taken up by plants, returned to the atmosphere via denitrification as NO, N_2O, or N_2 gas, or will be removed from the soil as NO_2^-, NO_3^-, or NH_4^+ in runoff to surface waters or leaching to groundwater (Nadelhoffer, 2001). Runoff of nitrogen from soils and direct deposition of ammonia to surface waters contributes to eutrophication of waterways and changes in aquatic ecosystems (de Boer, 2003; Krupa, 2003).

Since ammonia is the primary basic gas in the atmosphere, it readily reacts with strongly acidic species in the atmosphere such as nitric and sulfuric acid, to form ammonium salts, also known as secondary particles, fine particulate matter, or $PM_{2.5}$ (particles less than 2.5 microns in diameter). Due to their small diameter and increased atmospheric lifetime of approximately 15 days, these fine particulates are able to travel further distances than gas phase ammonia before being dry or wet deposited to the ground surface. Given the right climatic and atmospheric conditions, these small particles can travel from agricultural areas to pristine mountain ecosystems or urban locations where they can mix with other pollutants and accumulate in the atmosphere, contributing to smog and human respiratory health issues. Rocky Mountain National Park is a prominent example of the impact of nitrogen deposition on fragile mountain ecosystems (Fenn et al., 2003; Baron, 2006). Recent research has shown that the transport of ammonia gas and ammonium particles has contributed significant amounts of nitrogen to the Parks soils, changing plant species and native ecosystem balance (Fenn et al., 2006; Baron, 2006). It is currently unknown how much of this nitrogen is contributed from livestock systems, but research is underway to make that estimation.

Human Health Impact

Ammonia is a highly hydrophilic base that has irritant properties when inhaled which, when combined with water, can injure and burn the respiratory tract (Issley and Lang, 2001). The basic form of ammonia, ammonia hydroxide, dissolves in the water of mucus membranes, hydrolyzes and rapidly irritates tissues mainly due to the high pH that results (Zumdahl, 1997). Ammonia can also alter the uptake of oxygen by hemoglobin due to the increase of pH within the blood (Issley and Lang, 2001), which leads to decreased oxygenation of tissues and decreased metabolic function. When in fine particulate ($PM_{2.5}$) form, ammonium particles can pose a greater risk to human health. Such small diameter particles are able to be respired and travel deeply into lung tissue causing a variety of respiratory ailments such as bronchitis, asthma, and even heart disease. Due to the side effects of ammonia exposure over 25 ppm, the American Conference of Governmental Industrial Hygienists (ACGIH) has recommended an 8 hour maximum exposure limit of 25 ppm to protect against the chronic effects of ammonia exposure. A 15 min short term exposure limit of 35 ppm has been established by ACGIH and also adopted by OSHA to reduce irritant effects of ammonia exposure (i.e. eye and upper respiratory tract irritation). However, due to possible cumulative health effects over time, the recommended daily long term occupational exposure limit of ammonia for agricultural workers is 7 ppm (Donham et al., 2000) , and 300 parts per billion (ppb) for community exposure (community exposure must be stricter because communities contain very susceptible people such as the elderly and children) (Merchant et al., 2003). At moderate concentrations (50 to 150 ppm), ammonia exposure can lead to eye, throat and skin irritation as well as cough and mucous buildup. Prolonged exposure at this level can result in the transfusion of ammonia from the alveoli into the bloodstream and a subsequent disruption of oxygen uptake by hemoglobin. At high concentrations (>150 ppm) ammonia can scar lung tissue, cause lower lung inflammation and pulmonary edema. Exposure to high concentrations of ammonia (500 to 5000 ppm) will cause death in a relatively short time period from prevention of oxygen uptake by hemoglobin (Merchant et al., 2003). These levels are rarely found from livestock operations, but may occur in closed manure storage facilities and poorly ventilated buildings where ammonia concentrations can accumulate.

Ammonium Particulates and Nitric Acid

Emission Sources

Livestock operations and farming practices can be significant contributors to both primary and secondary atmospheric particulate matter (PM), also known as dust. Sources of primary particulate matter (course PM or PM_{10}, which are particles with a diameter between 2.5 and 10 microns) from animal agriculture include road dust, wind blown soil, feed dust, manure dust, and dust from drylots and other housing surfaces. Smaller particle sizes are known as secondary particulate matter or $PM_{2.5}$ (particles with a diameter less than 2.5 microns). Secondary particulates are particles formed in the atmosphere from gas-to-particle conversion processes during the reaction of gaseous species. The most common form of $PM_{2.5}$ emitted from livestock operations are ammonium salts produced from reaction of ammonia and acidic atmospheric species such as nitric and sulfuric acid. From both human health and environmental perspectives, ammonium salts ($PM_{2.5}$) are the most important particulate species emitted from livestock operations.

Ammonium (NH_4^+) is the ionic (solid or aqueous phase) form of ammonia (NH_3). It is produced when ammonia gains a hydrogen ion from an acid. Because it is a basic compound, ammonia is highly reactive with atmospheric acids such as nitric or sulfuric acid, both of which are emitted from combustion processes, and are present in the air plume around a livestock facility. Ammonia will rapidly react with these acids, forming ammonium sulfate preferentially, then ammonium nitrite. These particulate species are major contributors to smog and decreased atmospheric visibility.

In Colorado, the most prominent acidic gas that ammonia reacts with is nitric acid (HNO_3) to form ammonium nitrate (NH_4NO_3). Nitric acid is primarily produced from chemical reaction of NOx (NO_2 and NO) emissions with ozone (O_3) and the hydroxyl radical (OH·). NOx is primarily produced from high-temperature combustion processes, associated vehicles and industry. There are also significant sources of nitric oxide (NO) produced by biomass burning as well as from incomplete denitrification in soil (Finlayson-Pitts and Pitts, 2000). This is a significant source of NO and subsequent HNO_3 production in agricultural areas. Nitric acid is primarily produced in the atmosphere through the following two pathways (Finlayson-Pitts and Pitts, 2000; Godish, 2004):

Daytime:

$NO + O_3 \rightarrow NO_2 + O_2$

(or) $2NO + O_2 \rightarrow 2\ NO_2$

$$NO_2 + OH\cdot + M \rightarrow \mathbf{HNO_3} + M \tag{2}$$

Nighttime:

$NO_2 + O_3 \rightarrow NO_3\cdot + O_2$

$NO_2 + NO_3\cdot \rightarrow N_2O_5$

$$N_2O_5 + H_2O \rightarrow \mathbf{2\ HNO_3} \tag{3}$$

The daytime processes (2) tend to be the major source contribution of nitric acid, but the nighttime reaction produces a fair amount in urban areas where ozone (O_3) is still in high concentrations at night time. The characteristic timescale for production of nitric acid from NOx is on the order of about one day (Finlayson-Pitts and Pitts, 2000). Once it is formed, nitric acid is largely stable and relatively non-reactive. In the gas phase, nitric acid can contribute to wet or dry nitrogen deposition, with dry deposition being the dominant removal process in most climates. Nitric acid will remain in the gas phase until it reacts with a basic species like ammonia to form ammonium nitrate in the flowing gas-to-particle conversion reaction (Finlayson-Pitts and Pitts, 2000):

$$NH_{3\,(g)} + HNO_{3\,(g)} \rightarrow NH_4NO_{3\,(s,\,aq)} \tag{4}$$

This reaction (4) is rapid and readily occurs when nitric acid and ammonia come into contact. The resulting ammonium nitrate salt can either be present in the solid or aqueous phase. Since its deliquescence point at 25°C is 62% relative humidity (RH), we would expect to see NH_4NO_3 in solid form below a water vapor concentration corresponding to 62% RH, while above this RH, the solid particle dissolves to form a concentrated liquid solution (Finlayson-Pitts and Pitts, 2000). High RH coupled with low ambient temperature tends to favor the formation of aqueous ammonium particles because relatively less NHO_3 and NH_3 are found in the gas phase and more in the aqueous phase (Finlayson-Pitts and Pitts, 2000). Increasing relative humidity results in an increase of the liquid water content of particles due to a high hygroscopic absorbing capacity of aerosols which results in an increase in particle size (Beck et al., 2004). This is important for visibility because as particle size increases, the particle's ability to absorb and scatter light increases, resulting in a greater reduction in atmospheric visibility. Additionally, decreased temperatures correspond to a lower value for the dissociation constant of NH_4NO_3 (equilibrium constant that measures the propensity of particulate NH_4NO_3 to split into its gas phase components, NH_3 and HNO_3), shifting the equilibrium of the system toward the aerosol (NH_4NO_3) phase and increasing the particle mass of NH_4NO_3 (Seinfeld and Pandis, 1998).

Environmental Impact

Environmentally, $PM_{2.5}$ is a concern for atmospheric visibility and particle deposition in pristine and urban areas. Fine particulates (mostly size range 0.1 to 1.0 μm) are responsible for most light scattering, and to a lesser extent, absorption of light in the atmosphere, which reduces visibility leading to smog or haze (Finlayson-Pitts and Pitts, 2000). As relative humidity increases, this effect becomes greater due to particle growth and increased light scattering ability. In pristine areas where particle sizes tend to be below the effective light scattering range (< 0.1 μm), an increase in RH (~ 80%) will cause these small particles to grow and move into effective light scattering range, decreasing visibility in rural and pristine areas (Finlayson-Pitts and Pitts, 2000). In Colorado where RH is low for the majority of the year (< 50 %), the effects of decreased visibility are usually due to an increase in PM in the air.

On a global scale, aerosol particles in the atmosphere may actually be responsible for reducing the greenhouse effect. This occurs when particles scatter light back out to space instead of to the Earth's surface (Finlayson-Pitts and Pitts, 2000).The net effect of back scattering depends on the particle size and composition, and the direction (solar zenith angle) of the incident light. Particles less than 1.0 um are most effective at scattering light back to space and reducing the amount of solar radiation that reaches the Earth's surface (Seinfeld and Pandis, 1998). However, the warming effect of greenhouse gases on the Earth's energy balance is still far greater than the cooling effect that atmospheric particles may have (Seinfeld and Pandis, 1998). This is due to the long lifetimes of greenhouse gases (10 to 150 years) compared to particles (days to weeks), and the effect they exert 24 hours a day verses the daytime only effects of particles.

Particulates are eventually removed from the atmosphere via wet or dry deposition. Most course particles (>$PM_{2.5}$) have a short lifetime (minutes to days) and usually settle by dry deposition near their emission source. Because they have a longer lifetime than their constituent gases (days to weeks), fine particulates (< 2.5 μm) are able to travel longer distances before being deposited to Earth's surface, allowing them to affect a much larger area. Fine particulates produced from agriculture (i.e., ammonium salts) are able to travel by wind and rain to remote locations contributing to surface water eutrophication, soil acidification, and ecosystem degradation (de Boer, 2003; Krupa, 2003). Studies conducted at Rocky Mountain National Park have found that secondary ammonium particulates and other fine particulates ($PM_{2.5}$) have contributed to decreased visibility and soil acidification in the Park, causing changes in fragile mountain ecosystems (Baron, 2006).

Human Health Impact

The most important PM species emitted from a human health standpoint are those with particle diameters of 10 microns (PM_{10}) and under. These small particles are able to be respired and deposited in airways, with smaller particles (< 2.5 μm) reaching the lung alveoli and even transfusing into the bloodstream (< 1 μm). The health effects associated with fine PM include asthma, bronchitis, coughing, increased mucus production, and increased rates of cardiovascular disease and death (Merchant et al., 2003). Biologically-derived aerosols (bioaerosols), such as fecal and bacterial origin dusts, may have additional heath effects depending on the composition of the aerosol. Bioaerosols and endotoxins are of concern because they may carry pathogens or other health degrading particles, contributing to respiratory distress and disease (Pell, 1997; Sunesson et al., 2001). These constituents lead to increased rates of respiratory diseases such as asthma, chronic obstructive pulmonary disease (COPD), farmer's lung, and allergies. The EPA annual national ambient air quality standard is 50 μg m^{-3} for PM_{10}, and 15 μg m^{-3} for $PM_{2.5}$, but no occupational standards exist for endotoxin exposure (Merchant et al., 2003).

In communities near livestock operations, PM exposure levels can be episodic with short periods of high PM levels. Since the production of dust varies diurnally and seasonally, and exposure varies with wind direction and speed, the exposure to surrounding communities is variable. Additionally, the closer one is to a livestock operation, the greater the potential for exposure to PM because larger diameter (PM_{10}) particles tend to dry deposit close to their emission source.

Methane

Emission Sources

Globally, the EPA (2005) estimates that livestock contribute 30% of the total U.S. methane budget. The majority of that methane (75% or 21% of the total US methane budget) is produced during ruminant enteric fermentation. Enteric fermentation is the microbial digestion of cellulose material in the rumen, which is released as methane gas by eructation (belching). Because this is a nutritional process, the rate of enteric fermentation and subsequent methane emission is largely dependent on animal diet (Johnson and Johnson, 1995).

The other 25% of the methane emissions from livestock are produced from anaerobic decomposition of organic matter in manure and anaerobic waste lagoons, which contribute to 9.8% of the total US methane budget. If animal manure is allowed to dry in a drylot or pasture system, or is processed aerobically (i.e. composting), methane emissions from manure are minimal (Yamulki, 2006; Amon et al., 2006). It is when manure is stored in an anaerobic liquid system that methane emissions become significant (Amon et al., 2006). Due to a shift to larger operations and more liquid handling systems, the emission of methane from livestock manure management has risen 26% since 1990, mainly in dairy systems, which have seen an estimated 38% increase in methane emissions since 1990 (EPA, 2005).

Crop agriculture also produces a small amount of methane, approximately 4% of the total agricultural sector contribution, mainly from flood irrigation during rice cultivation (EPA, 2005). Additional sources of methane emissions include landfills, natural gas, anaerobic decomposition in swamps and lakes, automobile exhaust, biomass burning (Godish, 2004; EPA, 2005), and a recently determined source from terrestrial plants (Keppler et al., 2006).

Environmental Impact

Environmentally, methane is of great concern as an atmospheric pollutant due to its global warming potential as a greenhouse gas. The Earth's surface temperature is controlled by the solar energy input from the sun and the surface albedo of the planet (Finlayson-Pitts and Pitts, 2000). The surface albedo is the fraction of incoming solar radiation that is reflected back to space, which is greatly affected by atmospheric gases (Finlayson-Pitts and Pitts, 2000). Atmospheric gases absorb and re-emit solar radiation during which, part of the solar energy is converted to thermal energy. Under "normal" atmospheric conditions this balanced gaseous reaction keeps the atmosphere warm, allowing life to flourish on Earth. Any factor that alters the Earth's radiation balance, or the radiation received by the sun, can have an effect on climate change. The presence and increase of greenhouse gases in the atmosphere alters the radiation balance by trapping the surface radiation emitted by the Earth, increasing the amount of thermal energy in the atmosphere, thus warming the atmosphere and Earth's surface (Finlayson-Pitts and Pitts, 2000).

Due to its thermal absorption properties, and increasing concentration in the atmosphere (EPA, 2005), methane gas is one of the top greenhouse gases (the others are carbon dioxide and nitrous oxide) responsible for global climate change. Of all the greenhouse gases, methane contributes to 20% of the atmospheric radiative forcing, its influence being 23 times more powerful than carbon dioxide on global warming (IPCC, 2001).

Due to its extensive sources and relatively long lifetime (10 years), methane is being produced and stored in the atmosphere at a much faster rate than it can be consumed by soil and atmospheric reactions (Godish, 2004) increasing its atmospheric concentration on a relatively consistent basis. It is a relative relationship because the interaction between the sources and sinks of methane has created an inter-annual emission cycle, with some year's contribution higher than others (IPCC, 2001). This is due in part to uncertainties in assessing the emissions of highly variable sources (IPCC, 2001), as well as the change in atmospheric hydroxyl radical (OH•) concentration, which is the major sink process (almost 90% of total sink; IPCC, 1996) for methane in the atmosphere ($OH\bullet + CH_4 \rightarrow CH_3\bullet + H_2O$; Godish, 2004). The remainder of methane is removed through dry soil oxidation (5%), and transport to the stratosphere (7%) (IPCC, 1996). Despite these difficulties in assessing methane concentrations in the atmosphere, the EPA (2005) estimates that methane emissions have increased by 3.2% from the agricultural sector since 1990.

Human Health Impact

Methane gas is odorless and relatively nontoxic at the concentrations emitted from livestock operations. As a health concern, methane gas has little effect on either direct human exposure or long term health consequences. Rather, methane has secondary effects associated with global climate change.

Nitrous Oxide

Emission Source

Nitrous oxide (N_2O) is produced directly from the microbial processes of alternating nitrification and incomplete denitrification processes in soil and animal waste. Overall, a very small portion (< 0.05 %) of the nitrogen excreted by livestock is expected to convert to nitrous oxide in the waste management system (IPCC, 2006). For nitrous oxide emissions to occur, the manure must first be handled aerobically where ammonia is converted to nitrate via nitrification (5), and then handled anaerobically where the nitrates are converted to nitrogen gas via denitrification (6). Nitrification conditions usually occur in dry manure handling systems, such as composting of manure, and denitrification occurs in anaerobic processes like waste lagoons. The following pathways illustrate the microbial process of nitrification of ammonium to nitrate by nitrifying bacteria, and incomplete denitrification of nitrate to nitrous oxide by denitrifying bacteria:

Nitrification: $NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$ (5)

Denitrification: $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow \mathbf{N_2O} \rightarrow N_2$ (6)

The processes of agricultural tillage, fertilizer use, and animal waste treatment account for about 39% of total global nitrous oxide emissions (Oenema et al., 2001) and 68% of US nitrous oxide emissions (EPA, 2005). Agricultural soil management, including manure application to land, accounts for about 94% of those total emissions, while on-farm manure management contributes only about 4% of the budget (EPA, 2005). Oceans are an additional source of nitrous oxide, contributing approximately 30% of global emissions (IPCC, 2001). In addition to agriculture and soils, anthropogenic sources include biomass burning and industrial sources (IPCC, 2001).

Environmental Impact

Although the total atmospheric concentration of nitrous oxide is very small compared to carbon dioxide and methane, nitrous oxide is a very potent greenhouse gas that contributes to global climate change. While it only contributes to 6% of the total radiative forcing from greenhouse gases, it is over 296 times more effective than carbon dioxide at affecting global climate change (EPA, 2005) due to its very long atmospheric lifetime (about 150 years) and high thermal absorptivity (Godish, 2004). Its long lifetime is due to the fact that nitrous oxide has limited atmospheric sinks. Due to this, atmospheric nitrous oxide concentration is steadily rising at a rate of 0.7% yr^{-1} (EPA, 2005), and has increased by 17% since 1750 (IPCC, 2001). Some inter-annual variation in concentration has been observed, mainly due to changes in fertilizer use, decrease in biogenic emissions (i.e., biomass burning), and an increase in stratospheric losses due to volcanic-induced circulation (IPCC, 2001).

In addition to global climate change, nitrous oxide is a significant contributor to the depletion of stratospheric ozone; but on a local level, nitrous oxide is a relatively non-toxic gas and poses minimal concern to human health and other air quality concerns such as visibility or nitrogen deposition (Godish, 2004).

Carbon Dioxide

Emission Sources

Carbon dioxide (CO_2) is produced and emitted to the atmosphere by aerobic biological processes, combustion, and weathering of carbonates in soil and rock (Godish, 2004). The major sources of carbon dioxide are fossil fuel combustion (95% of total CO_2 budget), industrial processes, forest clearing, and biomass burning (IPCC, 2001; EPA, 2005). Since they are usually done in order to promote agriculture, forest clearing and biomass burning can be thought of as indirect impacts of animal agriculture. Animal agriculture directly contributes a very small amount (0.4% yr^{-1}; IPCC, 2001) to the carbon dioxide budget, and is not even considered by the EPA (2005) as a significant source of carbon dioxide in their analysis of greenhouse gas contributions by agriculture.

The major contribution of carbon dioxide from agriculture is animal respiration (Kinsman et al., 1995) and the burning of fossil fuels for power generation and transportation. Aerobic composting also contributes to carbon dioxide, but it is a small percentage (Hao et al., 2004). Agriculture can actually act as a sink for carbon dioxide by sequestering carbon and storing it in biomass and soils. Additional sinks include forests, oceans, and the atmosphere (IPCC, 2001; Godish, 2004).

Environmental Impact

Carbon dioxide is the most abundant of the greenhouse gases and contributes the major fraction (60%) to radiative forcing and the effects of global warming (IPCC, 2001; Godish, 2004). While it is not as potent a gas as nitrous oxide or methane, its long life time (approximately 100 years) and abundance of anthropogenic sources make it the most significant of the greenhouse gases. Current estimates indicate that global carbon dioxide emissions are increasing at a rate of 1.5 to 1.7 ppm_v per year (IPCC, 201). This is due to decreased terrestrial uptake from deforestation, increased fossil fuel use, and ocean uptake saturation (IPCC, 2001).

EMISSIONS FROM DAIRY OPERATIONS

Ammonia

Ammonia is one of the most heavily studied gases emitted from livestock operations. Its source concentrations have been characterized from barns, pastures, drylots, waste systems, and field application. Additionally, seasonal and diurnal fluxes in ammonia emissions from these sources have been documented. However, due to differences in management and density of livestock operations around the world, ammonia emissions are a regional issue, and exact emission factor values for an operation can be misleading. The following summary of data on trends and emissions of ammonia from dairy operations is based largely on percentage nitrogen loss by operation area (i.e. barns, drylot, lagoon, etc.). A summary of ammonia volatilization rates by operation area is given in Table 1.1.

Source Emissions

Ammonia volatilization from manure is directly related to an animal's nitrogen (protein) intake (Frank et al., 2002; Frank and Swensson, 2002; Cole et al., 2005; Todd et al., 2006). Of the total nitrogen excreted in manure (70% of the N intake, Wilkerson et al., 1997; or 29.5 kg hd^{-1} yr^{-1}, Webb, 2001), 41 to 54% is excreted as urinary urea nitrogen in lactating dairy cows (Wilkerson et al., 1997; James et al., 1999; Van Horn et al., 2004), and 72% of the urea is volatilized as ammonia (James et al., 1999). James et al. (1999) illustrated a significant difference in nitrogen excretion between heifers and mature cows, with heifers excreting about half the amount of urinary urea as mature cows. However, Wilkerson et al. (1997) found that while heifers excreted 25% less manure than lactating cows, the proportion of excreted nitrogen that was in urine was greater, 57 vs. 50%, respectively. Dry cows excreted half the amount of manure as lactating cows, but had a greater proportion of excreted nitrogen in their urine, 68% vs. 50%, respectively.

After it is excreted, Van Horn et al. (2004) estimated that 50 to 75% of nitrogen in manure is volatilized as ammonia prior to entering the waste management system. Since ammonia volatilization peaks 10 to 15 hours after excretion (James et al., 1999), manure not collected in this time period will experience high rates of ammonia loss in the housing area (barn or drylot), and lower rates in subsequent manure handling stages. Pollet et al. (1998) calculated an ammonia volatilization rate of 24 to 34% of total nitrogen deposited in dairy barns in the summer months in Belgium. Amon et al. (2001)

concluded that 42% of total ammonia emissions from a dairy system in Austria came from the housing. Moreira and Satter (2006) found that 38 to 50% (228 to 246 g hd^{-1} d^{-1}) of the total manure nitrogen excreted by dairy cows in a US freestall barn volatilized as ammonia in the summer months. Winter ammonia emissions were lower: 16 to 19% (99 to 119 g hd^{-1} d^{-1}) of the total nitrogen excreted in manure. For drylot operations, Todd et al. (2005) found that hydrolysis of urinary urea from drylot corrals was almost complete within 24 hours of deposition. Ammonia concentrations from urine patches ranged from an average low of 43 $\mu g\ m^{-3}$ in the winter to an average high of 129 $\mu g\ m^{-3}$ in the summer (maximum concentration was 257 $\mu g\ m^{-3}$), which represented an ammonia volatilization rate of 7 to 43%, respectively. The concentration of ammonia volatilized varied based on season and amount of dietary crude protein and subsequent nitrogen deposition by animals in the corral.

Amon et al. (2006) demonstrated that the amount of ammonia volatilized during storage directly influenced that amount volatilized during field application; the greater the loss during storage, the less loss at application. Different storage techniques such as aeration, covers, and biogas production, influenced the rate of ammonia volatilization, with untreated dairy waste lagoons volatilizing 18.1% (41.0 g NH_3 m^{-3} slurry) of total nitrogen as ammonia; the rest was volatilized during composting or field application. Amon et al. (2001) concluded that 20% of total nitrogen was lost during anaerobic manure storage. In an inventory of nitrogen loss from dairy operations due to ammonia volatilization during manure handling, the IPCC (2006) listed loss rates (%) for different sectors including: anaerobic lagoon, 35%; liquid/pit storage, 40%; dry lot, 20%; and solid storage (stockpile), 30%. The percent is the percent of total nitrogen entering the system that is volatilized as ammonia. Webb (2001) estimated that ammonia loss during combined housing and storage was 42.7% of the total nitrogen that entered the system. For composting, Hao et al. (2004) reported that of the initial nitrogen entering the compost, 41.5% was volatilized as ammonia, which represented about 95% of the total nitrogen losses from compost (the other 5% of gaseous N loss was from N_2O and N_2).

The portion of nitrogen that is not lost during housing or waste storage and treatments can be volatilized at field application. Amon et al. (2001) concluded that 38% of nitrogen in dairy manure is volatilized during manure field application. Sommer and Hutchings (2001) surveyed a variety of application techniques and found that cattle slurry emitted 40 to 67% of nitrogen as ammonia at application, and solid manure emitted 65% within 6 days. The rate of volatilization is highly dependent on climate and soil characteristics for which a variety of equations have been developed to predict ammonia emission from surface applied manures (Sommer and Hutchings, 2001).

Seasonal Profile

Ammonia has been found to have a distinct seasonal cycle with higher emissions in the warm months (spring, summer) and lower emissions in cooler months (fall, winter) (Robarge et al., 2002; Walker et al., 2004; Walker et al., 2006). This relationship has been demonstrated in lagoons (IPCC, 2006), composting (Amon et al., 2001), drylots (Todd et al., 2005), and housing barns (Zhang et al., 2005; Moreira and Satter, 2006). Walker et al. (2006) found a positive correlation between increasing temperature and ammonia concentration, which is consistent with the prediction that soil and manure ammonia emissions increase exponentially with temperature. Muck (1982) suggested that below temperatures of 10° C, urease activity, and subsequently ammonia volatilization, is very low. At temperatures above 30° C, essentially all urea in urine is hydrolyzed as ammonia within six hours of deposition to the barn floor (Muck, 1982). Smits et al. (1995) found that an increase in animal enclosure temperature from 10 to 24° C resulted in a 46% increase in ammonia emissions. Zhang et al. (2005) found a five fold increase in ammonia emissions from a flushed dairy barn in the same temperature range.

Season also has a large effect on the fraction of ammonia partitioned between the gas and particle phase downwind of agricultural sites. Walker et al. (2004) reported that the fraction of ammonia in the gas phase exceeded 50% in the summer months. This is partially because high temperatures and low relative humidity shift ammonium particle (NH_4NO_3) equilibrium such that the gas phase components, NH_3 and HNO_3 are favored. Thus more ammonia will be found in the gas rather than the particle phase in the warm months.

Diurnal Profile

Zhang et al. (2005) found the highest ammonia emission from dairy barns in the afternoon. This is expected since peak ammonia emissions occur 10 to 15 hours after excretion (James et al., 1999), and the majority of manure is deposited in the morning hours (0600 to 0700 h; Aland et al., 2002), which puts the peak of ammonia emissions around 1600 h. Additionally, temperature is usually highest in the afternoon, which is directly correlated to an increase in ammonia emissions (Aneja et al., 2001). In areas with high ammonia emissions, diurnal patterns are opposite of what is expected. Walker et al. (2004) found that ammonia concentration from swine facilities was higher at night, especially in the summer months. They postulate that this is likely the result of accumulation and inefficient vertical mixing of ammonia within a relatively shallow boundary layer. At sites with low ammonia emissions, higher concentrations were observed during the daytime (Walker et al., 2004). Some studies have found no clear diurnal pattern of ammonia emissions at all (Parmar et al., 2001; Robarge et al., 2002). This is likely due to the heterogeneous behavior of gaseous ammonia as a result of competition between upward diffusion into the atmosphere and deposition to the surface and particle conversion.

Vertical Profile

ApSimon et al. (1994) reported that the vertical behavior of ammonia was very difficult to model because the chemical reactions involving ammonia are highly variable over the boundary layer. Additionally, Walker et al. (2006) reported that ammonia concentrations at ground-level were highly variable with wind speed, likely the result of more efficient mixing of ground-level ammonia emissions at increased wind speeds. Despite these constraints, ApSimon et al. (1994) found that ammonia emissions decreased consistently and markedly in the atmosphere with height. In their study, the highest concentrations (18 $\mu g\ m^{-3}$) were found at ground level, as expected, and decreased to <1 $\mu g\ m^{-3}$ around 75 m, demonstrating a significant loss of ammonia in the atmosphere to transport, deposition, and particle conversion. Erisman et al. (1988) found similar results with ammonia concentrations highest at ground level (2m) and steadily decreasing up to 200 m with an average upward flux of 0.12 $\mu g\ m^{-2}\ s^{-1}$.

Ammonium Particulates

Source Emissions

Since ammonium particles are secondary particles formed by chemical reaction in the atmosphere, source emissions are difficult to quantify. In general, an increased emission of ammonia from a livestock operation will promote the formation of ammonium particles downwind. This is because production of ammonium aerosol is from reaction of ammonia and acidic atmospheric species (i.e. nitric and sulfuric acid), and is thus positively correlated with ammonia emissions (Walker et al., 2004). In areas of excess ammonia emissions, ammonium particulate production is limited only by the concentration of acidic species (HNO_3 and H_2SO_4) in background air.

Walker et al. (2004) reported a ratio for NO_3^- to NH_4^+ of about 0.03 for ammonium nitrate particulates downwind of an agricultural site; Robarge et al. (2002) found a ratio of 0.85, and Walker et al. (2006) 0.90. The large variability in ratios demonstrates the operational and regional variability in emissions for both ammonium and nitric acid.

Seasonal and Diurnal Profile

Ammonium shows a similar seasonal trend to ammonia with higher concentration values occurring during the warmer months (Robarge et al., 2002; Walker et al., 2004; Walker et al. 2006). Both Robarge et al. (2002) and Walker et al. (2006) reported that nitric acid also showed the highest concentrations at an agricultural site during the summer months. This is in part due to the equilibrium shift to gas phase NH_3 and HNO_3 at high temperatures, rather than solid or aqueous NH_4NO_3, which is favored during cooler temperatures and high relative humidity (Walker et al., 2006). Therefore, higher ammonium particle concentrations should be observed in the winter rather than the summer months. Unlike seasonal trends, neither Robarge et al. (2002) or Walker et al. (2004, 2006) found a significant diurnal pattern for ammonium.

Vertical Profile

Ammonium concentration has been shown to vary little with heights up to 200 m (Erisman et al., 1988; ApSimon et al., 1994). Measurements by Erisman et al. (1988) show that ammonium concentration varied by only 25% between 2 and 200 m with a slight decrease in concentration with height.

Nitric Acid

Source Emissions

There is little to no data on nitric acid emissions directly from livestock operations. Since nitric acid is primarily produced from chemical reaction of NOx (NO_2 and NO) with ozone (O_3) and hydroxyl radical (OH·), the only source of possible nitric acid production could be from the products of incomplete denitrification (NO_2 and NO) in anaerobic manure systems. The majority of denitrification processes tend to release nitric acid (N_2O) or N_2 gas, rather than NOx intermediates. Therefore, the production of nitric acid on farm is minimal, if not unlikely.

The presence of nitric acid is still important as a background species in ambient air that encounters dairy emissions. This is because nitric acid readily reacts with basic species like ammonia, which is emitted in large quantities from dairy operations, to form ammonium nitrate in a gas-to-particle conversion reaction (Finlayson-Pitts and Pitts, 2000). This reaction is rapid and readily occurs when nitric acid and ammonia come into contact.

Little information is available on the background concentrations of nitric acid in Colorado. A 1982 study by Cadle et al. measured nitric acid and ammonia in ambient air in Denver, Colorado and found that the average winter nitric acid concentration was 0.84 ppb, and ammonia concentration was 3.4 ppb. The authors cited feedlots as the source of ammonia, which was almost 50% higher than any other U.S. city monitored. Since then, NOx emissions have risen (EPA, 2003), so background nitric acid concentrations are most likely higher.

Seasonal and Diurnal Profiles

Parmer et al. (2001) reported a diurnal variation for nitric acid concentration with maximum levels in the afternoon (1200 to 1500 h) and minimum levels in the early morning. A seasonal variation was also recorded with maximum concentrations found in the winter months. This is unexpected since in cooler months, nitric acid is usually found in particulate form (NH_4NO_3) which is favored during cooler temperatures and high relative humidity (Walker et al., 2006). Following expected trends, both Robarge et al. (2002) and Walker et al. (2006) reported that nitric acid showed the highest concentrations at agricultural sites during the summer months.

Vertical Profile

Nitric acid has been shown to have a fairly consistent vertical profile up to 200m (Erisman et al., 1988; ApSimon et al., 1994). ApSimon et al. (1994) modeled the emission profile of nitric acid and found that emissions decreased sharply at ground level due to high surface deposition velocity, but after about 25 m, were stable, varying by only 1 to 2 μg m^{-3} up to 200 m. Erisman et al. (1988) showed similar results measuring decreasing nitric acid concentrations up to 25 m, and increasing concentrations above that. Authors suggest that the strong increase of concentration with height could be due to a reduction of reaction with ammonia and/or dry deposition. Ammonia concentration is so high near the ground surface that virtually all nitric acid can react with ammonia before it reaches the ground surface, hence, the decreased emissions reported below 25 m near the ground surface in both studies.

Methane

Global methane concentration has risen significantly over the last 200 years to a current background level of 1.847 ppm (1.319 mg m^{3-1} @ STP) in the northern hemisphere (CDIAC, 2006). The contribution of livestock to this value is approximately 20% (EPA, 2005) based on emissions from enteric fermentation and waste management (Table 1.2).

Source Emissions

The primary source of methane production from livestock is ruminant enteric fermentation, which represents 20% of the total methane emissions from anthropogenic activities and 75% of emissions from all agricultural sources (EPA, 2005). In the US, beef cattle contribute to 71% of the total enteric methane emissions, and dairy cattle 24% (EPA, 2005), mainly due to a larger population of beef cattle. Other ruminants (i.e. sheep, buffalo, etc.) contribute 4%, and non-ruminants 1% of the remaining methane budget. On a per head basis, dairy cattle produce more methane per head (121 kg CH_4 hd^{-1} yr^{-1}) than beef cattle (53 kg CH_4 hd^{-1} yr^{-1}) (IPCC, 2006), primarily due to differences in diet (Johnson and Johnson, 1995).

Lassey et al. (1997) measured methane emissions directly from lactating dairy cattle on pasture and found a mean emission rate of 229 to 313 g CH_4 hd^{-1} d^{-1} (94 ± 4 kg CH_4 hd^{-1} yr^{-1}). The emissions rate varied based on individual animal variation, season, and physiological state of the animals. DeRamus et al. (2003) also found a variation in methane emissions from pastured dairy cattle based on animal variation, season, and different dietary forages. They reported emissions of 86 to 193 g CH_4 hd^{-1} d^{-1} from heifers, and 120 to 255 g CH_4 hd^{-1} d^{-1} for mature cows. Dietary effects and animal variation in methane emissions from cattle have been well documented (Johnson and Johnson, 1995). McGinn et al. (2006) measured methane emissions from a whole dairy using tracer gas and modeling techniques and reported a value of 286 g CH_4 hd^{-1} d^{-1} from a mixed dairy herd.

The other 25% of the methane emissions from livestock is produced from anaerobic decomposition of organic matter in manure and anaerobic waste lagoons, which contributes to 9.8% of the total anthropogenic methane emissions (EPA, 2005). Dairy systems are the greatest contributor to methane emission from waste systems due to the liquid storage and anaerobic nature of waste lagoons (Phetteplace et al., 2001). For example, at 20° C, dairy lagoons emit 78 kg CH_4 hd^{-1} yr^{-1}, while solid manure management emits only 2 kg CH_4 hd^{-1} yr^{-1} (IPCC, 2006) only 3% of that from dairy lagoons. A similar difference was found by Amon et al. (2006) who looked at methane emissions from a variety of lagoon treatments and found that about 99% of methane emissions occurred during liquid storage of manure, and <1% occurred during composting or field application. Hao et al. (2001, 2004) confirmed that the emission of methane from compost was very low (0 to 0.04 kg C m^{-2} d^{-1}), between 2 and 3% of the initial carbon entering the compost, or 5 to 8% of total gaseous carbon loss. Yamulki (2006) reported that methane emissions accounted for only 0.02 and 0.06% of the total initial carbon in the compost. Additionally, Miller and Berry (2004) found that methane emissions from drylot surfaces were low, accounting for only 3% of total carbon emissions. These findings confirm that the majority (> 97%) of methane emissions from a dairy operation should come from the liquid manure treatment and storage areas.

Seasonal Profiles

The emission of methane from manure is highly dependent on temperature (Moller et al., 2004), with greater emission occurring at increased temperatures. Due to this, the IPCC (2006) gives methane emission factors from lagoons based on a temperature range of <10 to >28° C, which can represent almost a 50% difference in emissions. For liquid manure, Moller et al. (2004) found that cattle manure had the greatest methane losses when stored at 20° C. The temperature effect on solid manure storage is less defined due to the already low emission of methane from solid manure.

Nitrous Oxide

Source Emissions

Global nitrous oxide concentration has risen significantly over the last 200 years to a current background level of 319 ppb (0.626 mg m^{-3} @ STP) in the northern hemisphere (CDIAC, 2006). The processes of agricultural tillage, fertilizer use, and animal waste treatment account for about 39% of the total global nitrous oxide emissions (Oenema et al. 2001) and 68% of US nitrous oxide emissions (EPA, 2005); the US has a greater number of agricultural sources and employs practices which contribute to a higher nitrous oxide budget. Livestock manure management only contributes about 6% of the total nitrous oxide emission from agricultural sources (EPA, 2005).

Of the total nitrogen that is excreted by dairy cattle (29.5 kg N hd^{-1} yr^{-1}; Webb, 2001), only a small fraction is emitted as nitrous oxide (0.44 kg N_2O hd^{-1} yr^{-1} for dairy cattle in North America; IPCC, 2006). Most of that is emitted during manure management, which is a small fraction of the total nitrogen emitted from waste systems (<1%; Kulling et al., 2001). The IPCC (2006) reports that drylots emit 0.02 kg N_2O-N kg N $excreted^{-1}$, uncovered anaerobic lagoons 0.0001 kg N_2O-N kg N $excreted^{-1}$, passive windrow composting 0.01 kg N_2O-N kg N $excreted^{-1}$, and manure stockpiles 0.005 kg N_2O-N kg N $excreted^{-1}$. Kulling et al. (2001) reported that of the total nitrogen in dry manure, only 7 to 25% was emitted as nitrous oxide. Hao et al. (2001, 2004) found that measured nitrous oxide loss was 0.39 to 1.07% of the initial total nitrogen in compost, which represented only 1 to 6% of the total nitrogen (NH_3+N_2O+N_2) volatilized from the compost. Yamulki (2006) found that the addition of straw to compost reduced nitrous oxide emissions by 7 to 30%, but that gaseous emissions were only 0.3 to 0.7% of the initial nitrogen in the compost. Amon et al. (2006) reported nitrous oxide emissions from waste lagoons to be 7 to 12% of the total nitrogen emitted from lagoons.

Carbon Dioxide

Global carbon dioxide concentration has risen significantly over the last 200 years to a current background level of 377.3 ppm (740.86 mg m^{3-1} at 25°C and 1 atm) in the northern hemisphere (CDIAC, 2006).

Source Emissions

The major source of carbon dioxide emissions is fossil fuel combustion, which represents 95% of the total CO_2 budget (IPCC, 2001; EPA, 2005). Agriculture contributes a very small amount (0.4% yr^{-1}; IPCC, 2001) to the carbon dioxide budget, and animal agriculture is not even considered by the EPA (2005) as a significant source of carbon dioxide. The main emitters of carbon dioxide on a diary operation, besides emissions from vehicles, would be direct carbon dioxide exhalation from cows (Kinsman et al., 1995; Jungbluth et al., 2001) and composting (Hao et al., 2004). The production of carbon dioxide from compost results mainly from the oxidation of easily degradable carbon compounds in the aerobic processes. Paillat et al. (2005) found the emission of carbon dioxide from compost to be 0.2 g CO^2-C kg^{-1} Total C h^{-1}, or 44% of the total carbon entering the system. Hao et al. (2004) reported a total carbon loss of 34 to 52% as carbon dioxide.

MEASUREMENT TECHNIQUES

Animal feeding operations are very heterogeneous facilities physically, biologically, and chemically, with emissions showing diurnal, seasonal, and site specific variability. Measuring emissions from livestock operations can be difficult due to these parameters, as well as management and animal variation across facilities. Different methods have been used to measure source and whole plume emissions from animal operations with varied success for ammonia, ammonium, nitric acid, methane, and carbon dioxide.

Accurate quantification of ammonia can be challenging because ammonia is both a sticky gas that readily absorbs onto almost all surfaces and is very susceptible to climate changes such as temperature, wind speed, and relative humidity. Ammonium (NH_4^+), the ionic form of ammonia (NH_3), also has challenges associated with sampling. Ammonium is usually measured as a particulate which is composed of ammonia and nitric or sulfuric acid. The partitioning between the gas phase components (i.e., $NH_3(g)$ and $HNO_3(g)$) and the ammonium particle phase (i.e. $NH_4NO_3\,(s)$) depends on the ambient temperature and relative humidity, which determines the dissociation constant between the two phases (Finlayson-Pitts, and Pitts, 2000). Even after successful collection, ammonium particulates can dissociate on the sampling surface and volatilize (Park et al., 2004). This makes the handling of ammonium samples very important. Nitric acid does not have as many sampling difficulties as ammonia or ammonium, but it must be handled carefully after sampling to avoid evaporation from sampling surfaces (Karakas and Tuncel, 1997). Greenhouse gases (methane, carbon dioxide, and nitrous oxide) have fewer sampling difficulties because they are less volatile than ammonia or nitric acid and are relatively non-reactive. A variety of sampling techniques has been developed to measure ammonia, ammonium particulates, nitric acid, and greenhouse gases, and some newer methods have been developed to overcome some of the challenges associated with sampling of volatile species. The following is a discussion of various techniques and methodologies for sampling these species.

Filter Packs and Denuders

Integrated sampling of ammonia, ammonium, and nitric acid can be done with passive samplers, acid bubblers, filters packs, and denuders. All of these methods are simple to use to characterize ambient emissions in any location under most atmospheric conditions. Of all the listed methods, filter packs are more frequently used than denuders (Anderson and Hovmand, 1994) or other methods due to advantages in handling, maintenance, and sampling cost (Karakas and Tuncel, 1997). In a filter pack system, all three species, ammonia, ammonium, and nitric acid can be collected at once using a three stage filter pack (Karakas and Tuncel, 1997; Park et al., 2004). A two stage denuder with a filter pack and cyclone on it for sampling a specific particle size can also be used (Masia et al., 1994; Anderson and Hovmand, 1994; Baek et al., 2004). Typical filters used for collection (in order of collection) are Teflon for ionic and ammonium particulate species, nylon for collection of nitric acid, and cellulose or quartz coated with an acid (i.e. citric acid, phosphoric acid) for ammonia collection (Masia et al., 1994; Karakas and Tuncel, 1997; Park et al., 2004). Karakas and Tuncel (1997) found that the collection efficiency of nitric acid on untreated nylon filters was 98% in controlled laboratory trials. The filter pack and denuder methods have been shown to have good correlation ($r^2 = 0.90$) for ammonia and ammonium particle sampling in field studies (Andersen and Hovmand, 1994). However, in areas of high background ammonia, high temperatures, and low relative humidity, Andersen and Hovmand (1994) found that the filter pack tended to overestimate ammonia concentration by 10% over denuder concentrations. This could be due to evaporation of ammonia from ammonium particles collected on the preceding Teflon filter (Andersen and Hovmand, 1994; Karakas and Tuncel, 1997; Park et al., 2004). Karakas and Tuncel (1997) found that as ammonia concentration in controlled conditions increased from 300 to 700 μg, the collection efficiency of oxalic-acid coated cellulose filters decreased 10% from 95 to 85%. The authors speculated that this was due to retention of ammonia on the preceding nylon filter, which in field studies was sometimes up to 25% of the ammonia collected on the cellulose filter depending on temperature, relative humidity, wind speed, and wind direction. Additionally, saturation of the cellulose filter may have caused ammonia deposition on succeeding inline filters. In order to accurately estimate the total concentration of ammonia, Karakas and Tuncel (1997) suggest analyzing the Teflon, nylon, and cellulose filters separately for ammonia, otherwise total concentration could be underestimated. Unlike ammonia, Karakas and Tuncel (1997) found that nitric acid was not retained on preceding or succeeding filters. However, similar to ammonia, the authors found an artifact for gas-phase nitric acid when nitric acid volatilized from the ammonium nitrate particulates collected on the Teflon filter, erroneously increasing the concentration of nitric acid measurements. In turn, ammonium nitrate concentration on the Teflon filter will be lower than actual values due to volatilization of particle nitrate during sampling (Park et al., 2004). This artifact is particularly evident during the hot summer months at low humidity. However, if the concentrations of ammonia and nitric acid at the sampling site are high enough to cause saturation with respect to ammonium nitrate aerosol formation, this error is minimized (Karakas and Tuncel, 1997). Shorter sampling times to reduce filter saturation also minimize this artifact error (Karakas and Tuncel, 1997). In general, the amount of ammonium nitrate particulates collected on the Teflon filter expressed in terms of gaseous pollutants was about 10% of the ammonia collected on the acid treated cellulose filter, and 12% of the nitric acid collected on the nylon filter (Karakas and Tuncel, 1997). The disadvantage of the filter pack method is the separation principle, which can lead to sampling artifacts from evaporation of ammonia or nitric acid from ammonium particulates (Anderson and Hovmand, 1994; Karakas and Tuncel, 1997; Park et al., 2004). Changes in humidity or temperature might change the equilibrium for ammonium nitrate aerosols collected on Teflon filters, causing evaporation of ammonia or nitric acid gas from the filter and leading to an overestimation of the gas phases (Anderson and Hovmand, 1994; Karakas and Tuncel, 1997; Park et al., 2004). Due to difficulties with the filter pack method, Anderson and Hovmand (1994) found that the precision error of the filter pack method was 10-20%. Additionally, these methods are very limited in their ability to characterize emissions with high resolution since they are single point samples. Increased resolution could be accomplished by changing out samplers more often, which increases sample analysis numbers and cost.

Flux Chambers

In order to quantify flux of surface emissions, flux chambers and evacuated canisters are utilized. Flux chambers are enclosed devises that measure surface gas emissions from a defined surface area. The system works by adding clean, dry sweep air into the chamber at a controlled rate, which is based on the chamber volume and sampling time (Kienbusch, 1986). The sweep air mixes with the surface emissions, and the species of interest is measured at exit from chamber. Flux chambers can be connected to acid bubblers, tedlar bags, suma canisters, syringes, or real time analyzers to collect gas samples directly from solid or liquid surfaces (Gholson et al., 1991; Eklund, 1992). A number of gaseous species can be collected using flux chambers including ammonia (Aneja et al., 2000; Sommer et al., 2006), volatile organic compounds (Gholson et al., 1991; Eklund, 1992), nitrous oxide (Hutchinson and Moiser, 1981; Jury et al., 1982), carbon dioxide, and methane (Sommer et al., 2004). Flux chambers are good at measuring surface emission flux, but can be limited in their ability to get a representative sample of a large area due to limitations associated with long sample times and a small sampling surface area (Eklund, 1992). Additionally, flux chambers must be handled properly to avoid sampling errors. Chambers must contain a properly sized vent tube/hole and be sufficiently sealed to the ground surface in order to minimize gaseous loss and sampling errors (Hutchinson and Livingston, 2001). Chambers are also prone to accumulating condensation on the inside if not handled properly, which will act as a sink for gases such as ammonia, decreasing the ambient concentration measured.

Remote Sensing

Methods have been developed including remote sensing techniques such as open-path Fourier transform infrared (FTIR) spectroscopy (Shores et al., 2005), differential optical adsorption spectroscopy (DOAS) (Rumburg et al., 2004), and tunable diode laser systems (Laubach and Kelliher, 2005) which are able to determine emissions from large area sources such as lagoons, drylots, and fields. These methods can characterize a heterogeneous emission source with high temporal resolution and good accuracy. Their main limitation is that they must have a clear, unobstructed path over the emission source making measurements in buildings (barns) and over a large area of a farm difficult. McGinn et al. (2006) tried to overcome this problem by incorporating inverse-dispersion calculations into tracer gas collection with open-path lasers. While they had good collection of methane from a whole farm, they also had problems with wind speed, wind direction, and inaccuracies with WindTrax modeling software.

Modeling

Models have been developed to try to overcome the limitations of measurement systems, and characterize both nitrogen and greenhouse gas species emissions qualitatively and quantitatively. Some models work on characterizing parts of an operation such as composting (Liang et al., 2004), buildings and barns (Quinn et al., 2001; Vranken et al., 2004), animals (IPCC, 2006), or animal excreta (Kebreab et al., 2004), while others aim at characterizing the entire system (Kohn et al., 1997; Pinder et al., 2004b). Most models use data from the literature or from field trials (obtained using the methods discussed above) to create estimates of emissions from livestock operations (Pinder et al., 2004a; Flesch et al., 2005). A user inputs data about their system and management techniques, and the model predicts the desired emissions based on these criteria. The major limitation here is that no current model is able to integrate all of the management variations that will influence emissions, nor do they account for climatic variables, both of which will greatly affect emission concentrations and profiles (Robarge et al., 2002).

Need for Alternative Techniques

The major limitation of the methods discussed above is that they can not give an accurate overview of the entire livestock operation, but rather just snapshots of pieces of the whole system. In order to characterize emissions from the entire system, a method that samples downwind of the operation at various heights with a high temporal resolution is necessary. The majority of studies conducted on animal feeding operations have looked at emissions no higher than 5 m (5m, Quinn et al., 2001; 2.6 m, Robarge et al., 2002; 2.4 m, Sommer et al., 2004; 5.2 m, Laubach and Kelliher, 2004). Quinn et al. (2001) stated that ammonia concentrations from a livestock building didn't vary greatly with height and that peak ammonia concentrations were measured at a height of 4 to 5 m. However, authors did not measure higher than 5 m, so this conclusion could be inaccurate. Emissions of most gases will still be present above 5 m, but will vary based on wind speed, atmospheric stability, and temperature (Marcillac et al., 2006). ApSimon et al. (1994) modeled ammonia and nitric acid gases in the atmosphere and showed that while both decreased with height, significant concentrations were still present up to 75 m. Additionally, Erisman et al. (1988) found that ammonia decreased steadily with increasing height up to 200 m, but concentrations were still 25% of ground level (2m) concentrations at this height. They also showed that nitric acid concentrations decreased up to 25 m and then increased with height up to 200 m. Ammonium showed a consistent decrease with height up to 200 m, but it was not significant. These studies show that significant concentrations from livestock operations can be found above 5 m. No reported system has been used on livestock operations to measure concentrations at heights above 10 m; therefore, a new and unique sampling methodology needs to be developed to account for vertical emission profiles from livestock operations. This will aid in understanding the behavior of emissions from livestock operations and can aid in modeling efforts to predict atmospheric transport of emissions and exposure to surrounding communities.

Table 1.1. Summary of ammonia emission sources and strengths

Measurement	%	Value (unit)	Source
Mean total manure production for dairy cow		68 kg cow^{-1} d^{-1}	Kulling et al., 2001
		50 to 60 kg cow^{-1} d^{-1}	Pollet et al., 1998
Amount of dietary nitrogen excreted in manure	70	106 kg cow^{-1} yr^{-1}; 0.2629 kg cow^{-1} d^{-1}	Wilkerson et al., 1997; Webb, 2001
Amount of excreted nitrogen as urinary urea nitrogen	41-54		Wilkerson et al., 1997; James et al., 1999; Van Horn et al., 2004
Amount of total manure nitrogen volatilized as ammonia	72		James et al., 1999
Amount of N volatilized as ammonia from dairy barn	24-34		Pollet et al., 1998
	38-50	228-246 g hd^{-1} d^{-1} (Summer)	Moriera and Satter, 2006
	16-19	99-119 g hd^{-1} d^{-1} (Winter)	Moriera and Satter, 2006
	42		Amon et al., 2001
Amount of N volatilized as ammonia from drylot corrals	20		IPCC, 2006
	43.5	129 μg m^{-3} (Summer)	Todd et al., 2005
	28.3	43 μg m^{-3} (Winter)	Todd et al., 2005
Amount of total N volatilized as ammonia from anaerobic waste lagoon	20		Amon et al., 2001
	18.1	41 g NH_3 m^{-3} slurry	Amon et al., 2001
	35		IPCC, 2006
Amount of total N volatilized as ammonia from compost/stockpile	30		IPCC, 2006
	41.5		Hao et al., 2004
Amount of total N volatilized as ammonia during field application	38 (liquid)		Amon et al., 2001
	40-67 (liquid)		Sommer and Hutchings, 2001
	65 (solid; after 5 days)		Sommer and Hutchings, 2001

Table 1.2. Summary of methane emission sources and strengths

Measurement	%	Value (unit)	Source
Amount of methane emitted from enteric fermentation in dairy cows	75	121 kg CH_4 $hd^{-1}yr^{-1}$	EPA, 2005; IPCC, 2006
		94 kg CH_4 $hd^{-1}yr^{-1}$ (229-313 kg CH_4 $hd^{-1}d^{-1}$)	Lassey et al., 1997
		43.8 to 93 kg CH_4 $hd^{-1}yr^{-1}$ (120 to 225 kg CH_4 $hd^{-1}d^{-1}$)	DeRamus et al., 20003
		104.4 kg CH_4 $hd^{-1}yr^{-1}$ (286 kgCH4/hd/d) (mixed herd)	McGinn et al., 2006
Amount of total carbon emitted as methane from drylots	3		Miller and Berry, 2004
Amount of total carbon emitted as methane from anaerobic lagoons	97	78 kg CH_4 $hd^{-1}yr^{-1}$	IPCC, 2006
	99		Amon et al., 2006
Amount of total carbon emitted as methane from compost	4	2 kg CH_4 $hd^{-1}yr^{-1}$	Amon et al, 2006; IPCC, 2006
	2 to 3	0 to 0.04 kg C m^{-2} d^{-1}	Hao et al., 2001, 2004
	0.02 to 0.06		Yamulki, 2006

CHAPTER II

REVIEW: STRATEGIES TO REDUCE AMMONIA, NITROUS OXIDE, AND PARTICULATE MATTER EMISSIONS FROM DAIRY AND FEEDLOT OPERATIONS

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ABSTRACT

Nitrogen emissions from dairy and beef feedlot operations have become a serious issue due to both environmental and health effects associated with those emissions. In the US, animal agriculture is a significant contributor to ammonia, nitrous oxide, and particulate matter. Various management strategies and technologies have been scientifically tested and proposed for control of these emissions. Preceded by a summary of their sources, health, and environmental impacts, a review of current methods available for mitigation of ammonia, nitrous oxide, and particulate matter is presented by areas of nutrition, animal housing, drylots, and waste management. The most feasible and economically viable solutions for emissions reduction have been presented as best management practices (BMPs) for use to reduce atmospheric emissions from dairy and feedlot operations. While many suggested BMPs will reduce emission of a select pollutant, they may also increase emissions of another. Therefore, BMPs must be carefully chosen based on a producer's reduction goals as well as economic feasibility and ease of implementation. Even with the proper use of BMPs, there will be some inevitable losses of gases from livestock operations. BMPs aid in mitigating losses and redirecting those inevitable losses to the least damaging pathways.

Keywords: Best management practices, Dairy, Feedlot, Ammonia, Nitrous oxide, Particulate matter

INTRODUCTION

Cattle operations, including dairies and feedlots, have been identified as major sources of nitrogen and particulate matter (PM) emissions more often in recent years. With the increasing proximity of agriculture and urban communities, agricultural operations are being acknowledged more frequently as sources of odor and human health concern (Shiffman, 1998; Shiffman et al., 1995, 2000; Merchant et al., 2003). Studies also note the impact of livestock emissions on global climate change, vegetation changes, soil acidification, water eutrophication, and natural ecosystem impacts (Nadelhoffer, 2001; de Boer, 2003; Krupa, 2003). In Colorado, Rocky Mountain National Park is a prominent example of the impact of nitrogen deposition on fragile mountain ecosystems (Fenn et al., 2003; Baron, 2006). Animal agriculture, in particular dairy and feedlot operations, has been credited as a significant contributor to those nitrogen emissions, which include ammonia and ammonium particulates, both of which are emitted in large quantities from livestock operations (EPA, 2005; Marcillac et al., 2006). Additionally, cattle operations have been recognized for years as a significant contributor of nitrous oxide (IPPC, 2006), a potent greenhouse gas produced during biological manure processes.

Dairy and feedlot operations emit a variety of emissions (ammonia, nitrous oxide, particulate matter) that can be directly or indirectly harmful to humans and natural ecosystems. Each atmospheric pollutant has its own sources, mitigation techniques, and reduction challenges. Whereas, ammonia and particulate matter are considered a regional problem, nitrous oxide contributes to global climate changes. Additionally, fine PM (particulate matter less than 2.5 μm in diameter), produced from ammonia, has serious health effects (Merchant et al., 2003). This makes regulation of these pollutants a different priority for local, state, and national governments. Since cattle operations are a significant contributor to ammonia, nitrous oxide, and PM, reduction strategies are needed to help reduce livestock's impact on environmental systems and human health.

We conducted a literature review of relevant practices available to reduce emission of ammonia, nitrous oxide, and PM from dairy and feedlot operations in viable and economically feasible ways. Listed as best management practices (BMPs), we reviewed practices that could help reduce emissions on cattle operations from animal nutrition, animal housing, drylots, and waste management systems. These areas were chosen because they are the most significant sources of emissions on livestock operations and have the greatest reduction potential for BMPs. For best management practices to succeed, they require the consideration of all relevant pollutants and a defined reduction goal in order to be implemented into an operation.

AMMONIA

Globally, animal agriculture is the largest source of atmospheric ammonia, accounting for approximately 40% of the total global emissions, and 70% of the total U.S. ammonia emissions (EPA, 2005). Of all the emissions considered from animal agriculture, ammonia is one of the most prominent gaseous species emitted from livestock operations and is heavily discussed in the literature from a management and environmental impact perspective.

Ammonia is produced on cattle operations when urea in urine combines with the urease enzyme in feces or soil and rapidly hydrolyzes to form ammonia gas. The reaction is quick, taking anywhere from 2-10 hours for ammonia volatilization to peak after mixing of urine and feces (Muck, 1981; James et al., 1999). The quantity and rate of ammonia volatilization from manure depends on a variety of factors such as the amount of crude protein in feed rations (Cole et al., 2005), manure management strategies (Rotz, 2004), pH (Aneja et al., 2001), and climate effects (i.e. temperature, relative humidity, wind speed) (Smits et al., 1995; Aneja et al., 2001).

Environmental Impact

In the summer months, ammonia concentrations downwind (200 m from source) from a dairy can reach up to 500 ppb during the hottest part of the day (Marcillac et al., 2006), which may only represent about 82% of the ammonia concentration at the source (McGinn et al., 2003). Source emissions (i.e. barns, drylots, and lagoons) can be much higher, reaching levels of over 20 ppm in heavily manured areas (Koerkamp et al., 1998).

When in gaseous form, ammonia has a relatively short atmospheric lifetime of about 24 hours, it usually deposits near its source, contributing to eutrophication of surface waters, soil acidification, vegetation changes, and changes in mountain ecosystems (de Boer, 2003; Krupa, 2003). Since ammonia is the primary basic species in the atmosphere, it readily reacts with strong acidic species such as nitric and sulfuric acids, which are byproducts of vehicle and industrial combustion processes. The reaction forms secondary particles known as ammonium salts, also referred to as fine particulate matter or $PM_{2.5}$ (particles less than 2.5 microns in diameter). Due to their small diameter and increased atmospheric lifetime of 15 days, these particulates are able to travel long distances before being dry or wet deposited to the ground surface. Given the right climatic and atmospheric conditions, these small particles can travel from rural areas to pristine mountain or urban locations where they can mix with other atmospheric pollutants and accumulate, contributing to smog and respiratory human health issues.

Human Health Impact

When ammonia is in fine particulate form, ammonium particles pose a great risk to human health because they are able to be respired and travel deep into lung tissue causing a variety of respiratory ailments over time such as bronchitis and asthma (Merchant et al., 2003). As a gas, ammonia has more acute short term effects. At moderate concentrations (50 – 150 ppm), ammonia gas exposure can lead to eye, throat and skin irritation as well as cough and mucous buildup. Prolonged exposure at this level can result in the transfusion of ammonia from the alveoli into the bloodstream and a subsequent disruption of oxygen uptake by hemoglobin. At high concentrations (>150 ppm) ammonia can scar lung tissue, cause lower lung inflammation and pulmonary edema. Exposure to high concentrations of ammonia (500 - 5000 ppm) can cause death in a relatively short time period from prevention of oxygen uptake by hemoglobin (Merchant et al., 2003). These levels are rarely found near livestock operations, but may occur in closed manure storage and poorly ventilated buildings where ammonia concentrations can accumulate.

NITROUS OXIDE

Nitrous oxide is a very potent greenhouse gas that contributes to global climate change and is over 206 times more effective than carbon dioxide at increasing global temperatures (Godish, 2004). It is produced directly from alternating nitrification and denitrification process in soil and animal waste. The processes of agricultural tillage, fertilizer use, and animal waste treatment account for about 39% of total global nitrous oxide emissions (Oenema et al. 2001). Agricultural soil management accounts for about 94% of those total emissions, with manure management contributing about 4% of the nitrous oxide budget (EPA, 2005).

Environmental Impact

Although the total atmospheric concentration of nitrous oxide is very small compared to carbon dioxide and methane and can be measured in the parts per billion (ppb), it contributes over 6% of the warming effect of all greenhouse gases (Dalal et al. 2003) due to its very long atmospheric lifetime (about 150 years) and high thermal absorptivity. Additionally, nitrous oxide is a significant contributor to the depletion of stratospheric ozone; but on a local level, nitrous oxide is a relatively non-toxic gas and poses minimal concern to human health and other air quality concerns such as visibility or nitrogen deposition.

PARTICULATE MATTER

Particulate matter is a concern for both atmospheric degradation and human health. Livestock operations and farming practices can be significant contributors to atmospheric particulate matter (PM), also known as dust. Sources of primary particulate matter from livestock facilities include feed dust, manure dust, dust from drylots, and road dust. These particles are generally larger than 10 microns in diameter (PM_{10}). Secondary particulate matter is produced from livestock operations by the chemical reaction of ammonia and acidic atmospheric species to form ammonium salts also known as $PM_{2.5}$ (particles with a diameter less than 2.5 microns).

Environmental Impact

Environmentally, fine particulate matter (particles with a diameter < 2.5 μm) is a concern for atmospheric visibility and smog in pristine and urban areas. $PM_{2.5}$ contributes to smog or haze by absorbing light and creating a visual barrier. Fine particulates can also travel by wind to remote locations and depending on their composition (i.e. ammonium salts), contribute to surface water eutrophication and ecosystem degradation (de Boer, 2003; Krupa, 2003). Studies conducted at Rocky Mountain National Park have found that secondary ammonium particulates and fine particulates ($PM_{2.5}$) have contributed to decreased visibility in the park and soil acidification, causing changes in fragile mountain ecosystems (Baron, 2006).

Human Health Impact

From a human health standpoint, the most important PM species emitted are those with particle diameters of 10 μm (PM_{10}) and under, which accounts for about one-third of all dust emitted from livestock operations. These particles are able to be respired and deposited in airways, with smaller particles (< 2.5 μm) reaching the lung alveoli and even transfusing into the bloodstream (< 1 μm). The health effects associated with fine PM include asthma, bronchitis, coughing, increased mucus production, and increased rates of cardiovascular disease and death. Biologically-derived aerosols (bioaerosols), such as fecal and bacterial origin dusts, may have additional heath effects depending on the composition of the aerosol. Bioaerosols are of concern because they may carry pathogens, endotoxin, or other health degrading particles, contributing to respiratory distress and disease (Pell, 1997; Sunesson et al., 2001). These constituents lead to increased rates of asthma, farmer's lung, allergies, cough, dyspnea (difficulty breathing), and development of other respiratory effects.

EMISSION REDUCTION STRATEGIES (BMPS)

Animal Nutrition BMPs

A summary of BMPs discussed for nutritional reduction of ammonia, nitrous oxide and particulate matter emissions is presented in Table 2.1. The relative reduction potential is illustrated along with cost of implementation and practicality of the BMP. The effects of the BMP on ammonia, nitrous oxide, and particulate matter are also included to show the connectivity of mitigation techniques on the entire system rather than just one species. Following is a review of nutritional related practices that could reduce emissions of ammonia, nitrous oxide and particulate matter.

The easiest and most effective way of reducing ammonia volatilization from dairy and feedlot operations is with proper animal feeding and management. Excess nitrogen fed to animals is excreted in the waste and readily volatilized as ammonia. For example, in high producing dairy cattle fed typical diets, up to 69% of the nitrogen consumed is excreted (Wilkerson et al., 1997), with most of that nitrogen (62%) excreted in the urine as urea nitrogen (Misselbrook et al., 2005). Through various management techniques, this excretion amount can be reduced, but the theoretical maximum efficiency is about 50%

nitrogen retention (Rotz, 2004). Beef cattle experience a similar inefficiency in nitrogen utilization, excreting as much as 80% of dietary nitrogen (Rotz, 2004). Therefore, matching an animal's nitrogen intake to its production needs is critical in reducing nitrogen excretion.

Nitrogen excretion is directly related to an animal's protein intake; therefore, targeting protein intake can optimize production while reducing nitrogen excretion and subsequent ammonia volatilization. Studies have shown that there is a direct correlation between the amount of crude protein in the diet, the amount of nitrogen excreted, and the amount of ammonia volatilized from manure; a reduction in crude protein in the diet leads to a reduction in ammonia volatilization from manure (Frank et al., 2002; Frank and Swensson, 2002; Cole et al., 2005; Todd et al., 2006). Frank et al. (2002) reported a 33% decrease in ammonia emissions from dairy manure when the protein in the diet was reduced from 19 to 14%. Cole et al. (2005) found that by reducing dietary crude protein level from 13 to 11.5%, beef steers had reduced nitrogen excretion and decreased ammonia volatilization from manure, while maintaining performance levels. Feeding less crude protein not only reduced the amount of total nitrogen in the manure in these studies, but it also changes the partitioning of nitrogen between the urine and feces. Since urinary nitrogen contains 60 to 70% of the total nitrogen excreted, mainly in the form of urea (Misselbrook et al., 2005; Todd et al., 2006), it is the main component in manure affecting ammonia volatilization. Todd et al. (2006) concluded that steers fed a reduced crude protein diet had 27% more nitrogen in the feces, 28% less nitrogen in the urine, and 44% less total ammonia loss from the manure. Todd et al. (2006) showed that decreasing protein intake will decrease the amount of ammonia volatilized from the manure by decreasing the excretion of urea nitrogen and retaining more nitrogen in the feces. Reducing the amount of nitrogen volatilized from manure can have beneficial effects later in the system when manure is applied to crops by improving the N:P ratio. Reducing the amount of protein fed may also decrease the cost of the ration, as protein is usually the most expensive part of an animal's diet. Additionally, this is a management practice that can be done in any region of the country without special modifications. Compared to other methods of ammonia reduction, reducing dietary crude protein may provide the most cost effective and practical method of reducing ammonia emissions from livestock operations. Additionally, any method that decreases animal nitrogen excretion, such as reduced protein intake, will aid in decreasing the overall nitrous oxide emission from a facility as well.

Group or phase feeding is a practice that helps reduce nitrogen by separating animals into groups by age, sex or stage of growth/production. Phase feeding allows animal dietary protein needs to be more precisely matched to their requirements. Cole et al. (2005, 2006) found that phase feeding decreased ammonia volatilization from beef feedyards by decreasing the amount of protein fed and increasing nitrogen utilization per group. However, they also found some detrimental effects on performance due to lower average daily gains. If average daily gain is reduced, animals will have to be fed longer to reach slaughter weight, and ammonia emissions per pound of meat could increase even though daily emissions may be reduced. This would suggest that proper ration nutrient balancing is necessary for each group.

Oscillating protein in the diet has been shown to be a means of reducing total nitrogen output in ruminants by increasing nitrogen retention; however, contradictory results have been found. Oscillating dietary protein works by changing the animal's protein intake amount from a low to a high amount every two to three days. Cole (1999) found that by oscillating dietary crude protein, lambs were able to retain more nitrogen and excrete less. However in studies with beef steers, Cole et al. (2003) found that oscillating protein in the diets increased nitrogen retention, but had little effect on overall nitrogen balance compared to cattle fed a consistent protein level. Archibeque et al. (2007a) found that steers fed an oscillating protein diet excreted less nitrogen in urine and had a subsequent lower ammonia volatilization than steers on conventional diets. Archibeque et al. (2007b) also found that steer performance was not compromised by the feeding of an oscillating protein diet. Cole et al. (2005) reported that the oscillating protein diet is most effective in ruminants fed a high concentrate diet. Oscillating protein is a fairly new method of feeding and still needs further research, but the potential benefits in reducing ammonia appear promising.

Compared to changes in the diet, relatively small reductions in nitrogen excretion can be made by increasing an animal's production efficiency. Increases in efficiency can be obtained through genetic selection, feed additives, handling, and animal environment changes. In cattle, production can be increased with the addition of hormones and various feed additives. Bovine somatotropin (bst) injections are given to dairy cattle to increase their milking efficiency, and have been shown to reduce nitrogen excretion by up to 7.8% (Dunlap et al., 2000). However, with growing concern for hormones and pharmaceuticals in soils and water supplies, the use of hormones in livestock is being selected against by a growing number of consumers.

Proper ventilation in buildings and frequent removal of manure from pen surfaces and floors will help reduce the production of ammonia in an animal's immediate environment leading to healthier and more productive animals by decreasing the negative health effects of ammonia on the animals.

There are no nutritional strategies to improve emission of particulate matter directly from the animal. The only contribution would be to minimize feed dust by minimizing the physical processing of feed, storing feed in bunkers away from the wind, and choosing feedstuffs that do not have an excess amount of finely ground dust associated with them

Animal Housing BMPs

A summary of BMPs discussed for reduction of ammonia, nitrous oxide and particulate matter emissions from animal housing is presented in Table 2.2. The relative reduction potential is illustrated along with cost of implementation and practicality of the BMP. The effects of the BMP on ammonia, nitrous oxide, and particulate matter are also included to show the connectivity of mitigation techniques on the entire system rather than just one species. Following is a review of practices that could reduce emissions of ammonia, nitrous oxide and particulate matter from dairy housing.

In dairy barns, ammonia volatilization occurs soon after manure is deposited on the barn floor. Urine urea nitrogen mixes with the urease enzyme in feces and rapidly hydrolyzes to form ammonia gas. The rate of the reaction is a function of mixing time, temperature, relative humidity, and pH of the manure (Muck, 1982; Voorburg and Kroodsma, 1992). Each of these factors can be controlled to some degree in enclosed barns.

The easiest and most effective way to reduce ammonia volatilization from barn floors is by removing manure, the main source of ammonia, at frequent intervals. In dairy systems, the most common types of housing systems are freestall barns or drylots. In freestall barns, animals are housed in open barns with the ability to move freely in open alleyways between bedded cubicles, provided for resting, and the feeding area. Manure is deposited primarily in the concrete alleyways, and removed on a regular basis. Since the deposition of fresh manure is frequent, and mixing rate increased in these areas, ammonia volatilization can be very high in freestall barns. On average, 37 to 43% of the total nitrogen excreted by dairy cattle is volatilized from the freestall area (Moreira and Satter, 2006). The removal of manure by scraping or flushing has an impact on ammonia volatilization. Studies have found that scraping had little impact on reducing ammonia volatilization (Kroodsma et al., 1993; Braam et al., 1997; Morelra and Satter, 2006), as scraping tends to spread and distribute manure over the barn floor surface increasing its surface area and volatilization potential. Rather, flushing alleyways with fresh or recycled lagoon water was shown to remove deposited manure and reduce ammonia emissions by 70% immediately after flushing (Kroodsma et al., 1993). By increasing the rate of flushing from every 4 to every 2 hours, further ammonia reductions were seen (Kroodsma et al., 1993).

Modifications to the floor surface can also reduce ammonia production potential. Grading a 3% slope can channel urine away from feces, reducing the mixing potential and ammonia volatilization by 21% compared to solid level floors (Braam et al., 1997; Zhang et al., 2005). A double sloped floor with a urine gutter in the center that traps and channels urine away from feces was shown to reduce ammonia emissions by 50% compared to solid floors (Braam et al., 1997). For concrete floors, the addition of grooves in the concrete floor can further aid in channeling urine away from feces, thus reducing ammonia emissions. Slatted floors that collect and channel urine away from feces have also been shown to decrease ammonia (Zhang et al., 2005). By combining a slatted floor and a slurry channel that is flushed regularly, Hartung and Phillips (1994) reported reductions in ammonia emissions of up to 70%, and Zhang et al. (2005) a 50% reduction over solid floors. Zhang et al. (2005) also showed that the type of flooring system had little effect on nitrous oxide emissions.

While rarely used in U.S. dairy operations, an alternative to slatted floors is a deep litter system. These systems use a deep layer of bedding to separate out urine and feces to reduce ammonia emissions. In the litter, a complex process of aerobic and anaerobic degradation occurs, leading to both nitrification and denitrification processes. Groenestein and Van Faassen (1996) found that while deep layer bedding reduced ammonia by 50% compared to the use of slatted floors, due to denitrification the total nitrous oxide losses were greater with deep litter systems, leading to a more negative environmental impact from emission of greenhouse gases. This system is not used in commercial dairy barns, due to its inefficiency and issues related to disposal of the litter.

The use of bedding in simulated dairy barn floors has been evaluated by Misselbrook and Powell (2005) who looked at six different bedding types typically used in dairy barns (chopped straw, sand, pine shavings, chopped newspaper, chopped cornstalks, and recycled manure solids) and their impact on ammonia emissions. They found that physical structure and relative absorbance capacity were the two most important characteristics that influenced ammonia emissions from bedding. The recycled manure was the most absorbent, retaining 15 times more urine than sand, which was the least absorptive and thus had the lowest ammonia emissions. Recycled manure had the highest rate of ammonia volatilization likely because the urine stayed on the top of the manure surface where it was more susceptible to volatilization. With sand bedding, the urine percolated to the bottom of the pile, reducing the urine-air interface and decreasing ammonia emissions, making it a commonly used material in dairy operations in the U.S. After sand, pine shavings had the second lowest ammonia volatilization rate followed by chopped straw. Chopped newspaper, chopped cornstalks, and recycled manure all had similarly high levels of ammonia volatilization.

The rate of ammonia production from manure is very rapid, but can be altered with variations in temperature. Below a temperature of 10° C, urease activity is very low, but activity increases exponentially at higher temperatures (Muck, 1982; Zhang et al., 2005). At 30° C, essentially all urea in urine is hydrolyzed as ammonia within six hours of deposition to the barn floor (Muck, 1982). Smits et al. (1995) found that an increase in animal enclosure temperature from 10 to 24° C resulted in a 46% increase in ammonia emissions. By reducing the temperature in barns, ammonia volatilization can be reduced. Temperature can be controlled with swamp coolers in enclosed barns, or by allowing more natural ventilation to circulate through barns in the cooler months. Animal performance and welfare needs to be taken into account to ensure that animals are not housed below their thermoneutral zone. According to Young (1981), the minimum critical temperature a dairy cow at peak lactation can withstand is -25 °C. This temperature is well below suggested temperatures (< 10 °C) to reduce ammonia volatilization from dairy barns.

Scrubbing exit air from enclosed barns with bio-filters can remove ammonia from the exhaust air and reduce the atmospheric emission from barns (Hilhorst et al., 2002; Melse and Ogink, 2005). Melse and Ogink (2005) reported that the use of acid scrubbers and biotrickling filters removed ammonia from the exit air of swine and poultry barns with a removal efficiency of 96 and 78%, respectively. Proper ventilation through the barn will also help reduce ammonia accumulation and PM in certain areas of the barn. Hinz and Linke (1998) found that ammonia concentration differed by 30% from the center of a swine barn to the outside walls, and that the concentration was highly dependent on ventilation rate. Additionally, Hinz and Linke (1998) found that peak dust emission in swine barns occurred at feeding, reflecting an increase in animal activity, and the contribution of feed dust to the inside air. To reduce feed dust in enclosed buildings, ventilation rates can be increased during feeding events, or the feed can be treated with some kind of binding compound like fat or molasses to reduce dust emissions from feed. While few dairy barns are totally enclosed, the ones that are could benefit from this technology. Bio-filters and trickling filters are still relatively new methods to reduce/remove emissions from enclosed barns and need further research.

Drylot Corral BMPs

A summary of BMPs discussed for reduction of ammonia, nitrous oxide and particulate matter emissions from drylot corrals is presented in Table 2.3. The relative reduction potential is illustrated along with cost of implementation and practicality of the BMP. The effects of the BMP to ammonia, nitrous oxide, and particulate matter are also included to show the connectivity of mitigation techniques on the entire system rather than just one species. Following is a review of practices that could reduce emissions of ammonia, nitrous oxide and particulate matter from drylot corrals.

The greatest ammonia emissions from feedlots occur from the surface of open drylot pens. Bierman et al. (1999) reported that 57 to 67% of the total nitrogen excreted is volatilized by the time that feedlot pens are cleaned. Dairies that employ a drylot system also see the greatest ammonia emissions from drylot pen surfaces. By harvesting manure in more frequent intervals (every 2 to 3 months rather than industry standard of 6 to 12 months), ammonia volatilization can be reduced from drylots. Ammonia volatilization reduction practices need to be utilized in subsequent stages of storage in order to reduce total ammonia volatilization from the system.

Because the volatilization of ammonia is dependent on the mixing of urine (urea) and feces (urease), dispersing urination and defecation events might help reduce ammonia volatilization from a pasture oriented pen surface as seen with some dairy and cattle operations. This application is not necessarily applicable to drylot situations. White et al. (2001) found that dairy cows on pasture tended to concentrate elimination behaviors around the water trough during the summer months, as this was where they spent the majority of their time. They concluded that the number of elimination events that occurred in a location was highly correlated with the time spent at the location. Therefore, the deposition of manure (i.e., urine and feces combined) can be affected by the management and layout of the cattle's corral environment. White et al. (2001)

suggested designing pasture pens with water and feed troughs at opposite ends of the corral to distribute manure evenly. Armstrong (1994) recommended placing shade over the center of the corral to encourage cattle to move throughout the corral as the shade moves over the course of the day, again to aid in the distribution of manure.

The pH of the soil surface greatly affects the rate of ammonia volatilization. If the soil is acidic, a pH below 6, ammonia will mainly be found in its ionic form ammonium, and volatilization will be low. At a higher pH, above 8, ammonia will volatilize rapidly from the soil surface. A variety of surface amendments to reduce soil pH have been tested on feedlot and dairy pen surfaces to assess their ability to decrease ammonia emissions. Aluminum sulfate (alum) has been shown to be the most effective additive in reducing the surface pH and subsequent ammonia emissions (Shi et al., 2001; DeLaune et al., 2004). In a laboratory study, Shi et al. (2001) found that alum reduced cumulative ammonia emissions by 98% over a 21 day period. They also reported that calcium chloride was an effective amendment, reducing cumulative ammonia emissions by 77%. DeLaune et al. (2004) found that alum was the most effective treatment in reducing ammonia emissions from poultry litter, reducing emissions by 62% over the control. They also concluded that surface application, rather than incorporation was more effective at reducing ammonia volatilization from litter compost piles. Kithorne et al. (1999) found that calcium chloride applied at 20% reduced the ammonia volatilization of poultry manure by 90%, whereas a 20% alum application only reduced ammonia volatilization by 73%. Unlike alum, the calcium chloride treatment works primarily due to microbial inhibition, rather than by reducing pH, thus having a greater impact on the entire manure pile. While surface amendment studies are successful in laboratory settings, they have less success in field application, losing effectiveness over a short period of time and showing variable results. This is probably due to reapplication of manure on treated pen surfaces and animal hoof action breaking and removing the treated pen surface crust.

In addition to surface amendments that reduce the pH to reduce ammonia emissions, enzymatic treatments can be used to inhibit the hydrolysis of urine urea to ammonia by the urease enzyme in feces. Various urease inhibitors are available, but NBPT (N-(n-butyl) thiophosphoric triamide) seems to be the most effective in inhibiting the hydrolysis of urea (Zhengping et al., 1991). While enzymatic treatments may not be as efficient as acidifiers in decreasing ammonia emissions, Shi et al. (2001) found that enzymatic treatment with the urease inhibitor NBPT could reduce cumulative ammonia emissions by 65%. They also found that on a benefit-to-cost ratio, the NBPT treatment to feedlot surfaces was more cost effective than alum treatment, yet it was still an expensive amendment for a producer to install. Varel et al. (1999) found that the addition of NBPT to cattle pen surfaces reduced the amount of ammonia volatilized by retaining the urea in the manure. After 11 days, hydrolysis of the urea and subsequent ammonia volatilization began to occur and by day 28 all the urea had volatilized as ammonia. It was speculated that this was due to chemical breakdown of the urease inhibitors, requiring more frequent application to maintain effectiveness. An efficient, lasting, and cost effective surface amendment to reduce ammonia emissions still needs to be found. Currently, surface amendments may be effective on a very small scale, but this has little practicality in the current large-scale livestock industry.

Nitrification followed by denitrification in soil is responsible for the conversion of ammonium into nitrous oxide. A potential strategy for reduction of nitrous oxide emissions would be to reduce the rate or inhibit the nitrification process. Nitrification inhibitors (DMPP) have been studied for the application of cattle slurry to soil with some success (Hatch et al., 2005; Monteny et al., 2006). Hatch et al. (2005) found that the effectiveness of nitrification inhibitors in field conditions was 60% effective in reducing the production of nitrous oxide. However, they discovered that the reduction of nitrification preserved the majority of the nitrogen in slurry as ammonium, which enhances the volatilization potential of ammonia.

Frequent manure harvesting, increased stocking density, surface compaction, and surface water application have all been recommended to control dust emission from drylot pens (Carroll et al., 1974; Miller and Berry, 2005; Razote et al., 2006). Increasing the moisture content of the pen surface works by directly affect the binding of surface manure and soil particles to limit the production of dust. To achieve optimal dust reduction, without increasing odor production, a surface moisture level of 26% has been recommended (Miller and Berry, 2005). While the application of water to the pen surface is the most direct way to increase surface moisture, a variety of methods have been suggested including increasing stocking density, adding surface amendments (Razote et al., 2006), and increasing manure pack depth to increase surface moisture (Miller and Berry, 2005). Compaction of the manure surface in laboratory settings has also been shown to decrease PM_{10} emission from cattle pen surfaces by about 30% over no compaction (Razote et al., 2006). In the Eastern Plains of Colorado where water is scarce and evaporation rate high, application of water to the pen surface is not practical. Instead, proper pen management and design is the best management tool of choice. The application of moisture to the corral surface can also increase hydrolysis of nitrogenous compounds on the pen surface to form ammonia (Muck, 1982). This is due to the increased solubility of ammonia in water, which tends to accumulate in wet areas of the corral and volatilize when the surface begins to dry (Voorburg and Kroodsma, 1992). Razote et al (2006) suggested the use of a surface amendment (wheat straw or sawdust) to help decrease dust emission. With initial high application of the amendment they found up to a 76 and 69% reduction in dust, respectively, over control measures. However, under laboratory settings, Razote et al. (2006) found a decrease in amendment effectiveness over time as hoof action broke down the crop residues and increased dust emission.

Peak particulate levels from drylots have been reported in the evening for feedlots reflecting an increase in cattle activity (Mitloehner et al., 2002) and a change in wind patterns (McGinn et al., 2003). Therefore, correlating feeding times with peak animal activity in the evening has been shown to decrease dust generation in cattle feedlots (Mitloehner et al., 2002).

The addition of shade to a pen can reduce dust generation by encouraging animals to spend time in the shaded area, moving with the shade over the course of the day and concentrating their elimination behaviors throughout the pen (Armstrong, 1994). This will distribute urine and feces over a greater portion of the pen surface, increasing total pen soil moisture and binding particles together (Mitloehner et al., 2002). Mitloehner et al. (1999, 2002) have also shown that heifers provided with shade exhibit less dust-generating behaviors, such as agonistic and bulling behavior, thereby reducing airborne PM potential.

Waste Management System BMPs

A summary of BMPs discussed for reduction of ammonia, nitrous oxide and particulate matter emissions from waste management systems is presented in Table 2.4. The relative reduction potential is illustrated along with cost of implementation and practicality of the BMP. The effects of the BMP to ammonia, nitrous oxide, and particulate matter are also included to show the connectivity of mitigation techniques on the entire system rather than just one species. Following is a review of practices that could reduce emissions of ammonia, nitrous oxide and particulate matter from waste management systems.

Ammonia volatilization from manure is a very rapid process, peaking 10 to 15 hours after excretion with 90% of the total ammonia volatilizing within 26 hours (James et al., 1999). The storage and land application of animal waste are significant sources of both ammonia and odor. The method of waste management (i.e. composting, lagoons, etc.) used on a farm affects the rate of ammonia emission. The most common method of waste treatment for dairy systems is anaerobic lagoons, with 90% of dairies employing a lagoon storage system in the U.S. (Rumburg et al., 2004). This is because lagoons are relatively inexpensive, require very little maintenance, and have no additional treatment costs. However, anaerobic conditions favor the denitrification process, converting oxygen rich nitrogen, such as nitrate, to reduced forms like nitrous oxide and dinitrogen gas. Usually, ammonia and dinitrogen gas are the main emissions from lagoons, with nitrous oxide rarely seen (Harper et al., 2000; Flessa et al., 2002). Composting of solids has also become a common practice in the dairy and feedlot industry today, as it is an effective way to treat manure and make it into a usable and more profitable product.

Solid Separation

Many livestock operations practice some method of solid separation prior to storing liquid manure slurry in a lagoon. During solid separation, the liquid portion of the slurry is removed and the solid portion is left. Often this solid portion is composted or stockpiled. The types of solid separation vary, and include screens, earthen pits, leaky dams, presses, and others. On average, producers in Colorado report that their solid separation methods, which vary, will remove between 20-40% of the total solids in the slurry influent (personal communication). The remaining solids go into the lagoon where they settle to the bottom, or get bubbled to the top of the lagoon surface by methane and carbon dioxide bubbles produced by bacteria in the lagoon. The manure solids that are removed from the influent usually contain about 25% of the total manure nitrogen, with the remaining 75% of the nitrogen in the liquid portion of the slurry (Rotz, 2004). The more efficient the solid separation method is, the more nitrogen that can be removed in the solid portion of the slurry, and the less that goes into the lagoon. Reducing the amount of solids that go into the lagoon also reduces odor since about 40% of potential odor generating compounds are found in the solids (Zhang and Zhu, 2003). Therefore, technologies that increase the efficiency of solids removal from influent will aid in reducing subsequent ammonia and odor emissions form lagoons.

Lagoons and Slurry Storage

The rate of ammonia volatilization from lagoons will vary with temperature, nutrient load (solids), pH (Sommer and Husted, 1995), the presence of a cover or crust on the surface, and the aerobic/anaerobic status of the lagoon. After solid separation, 75% of the total nitrogen in collected manure goes into the lagoon with the liquid portion of the influent

(Rotz, 2004). At a typical lagoon pH of 7.0-7.6 throughout the year, 30 to 70% of the total nitrogen is expected to be volatilized as ammonia within the first 6 to 12 hours of storage, after which time volatilization decreases rapidly (Sommer and Hutchings, 1995). A portion of the remaining nitrogen in solution is either lost as nitrous oxide and nitrogen gas following nitrification/denitrification, or retained in the lagoon as nitrate or other non-gaseous nitrogen compounds (Harper et al., 2000). Since lagoon effluent is often re-used as flush water for dairy barns, the remaining nitrogen retained in the lagoon water is returned to the barns and usually volatilized as ammonia. Thus, with a recycling system, the nitrogen loss potential is near 100%. If the lagoon water is used for irrigation, this volatilization potential is less (about 50%) due to nitrogen application to fields (Rotz, 2004) and uptake by plants.

If the pH of the lagoon is maintained above 8 (basic), ammonia volatilization increases (Sommer and Husted, 1995) and ammonia volatilization may be up to 70% of the total nitrogen entering the lagoon (Rotz, 2004). At a pH below 6 (acidic), ammonia is bound in solution in its ionic ammonium form and little ammonia volatilization will occur (Aneja et al., 2001). Achieving a low lagoon pH requires the addition of acidifying compounds such as alum, citric acid, and nitric acid to the lagoon. Positive results have been found in reducing ammonia emissions from small-scale waste confinement and laboratory studies, but large scale studies are limited due to cost and feasibility on livestock operations. In addition, low pH reduces the efficacy of anaerobic lagoons and increases odor by decreasing the breakdown of odor compounds by microbes. The acidic lagoon water can also have detrimental effects when applied to crops later. Lefcourt and Meisinger (2001) showed that acidifying agents like alum have been shown to reduce ammonia volatilization from dairy slurry by 58% and soluble phosphorus by 75%, but increased soluble aluminum in solution, which led to soil acidity when slurry was applied to land. The addition of zeoilite as an alternative slurry additive was shown to reduce soluble phosphorus and ammonia emissions by 50% by sequestering ammonium-N (Lefcourt and Meisinger, 2001), which could be a good source of slow-release nitrogen for plants. In areas where soil is generally basic and has a good buffering capacity, the additional acidity of the slurry may not be a problem when applied to fields.

An increase in ambient temperature will further increase the rate of ammonia volatilization from waste lagoons (Harper et al., 2000; Aneja et al., 2001; Heber et al., 2002). Aneja et al. (2001) found a strong correlation between ambient temperature and ammonia flux from the surface of swine lagoons. They reported that the greatest emission of ammonia was in the summer months, which accounted for up to 60% of the total yearly flux. Safley and Westerman (1992) found a similar correlation between seasonality and ammonia emissions from dairy waste lagoons, noting that the greatest ammonia emissions were in the warmer summer months. Likewise, the lowest ammonia volatilization is in the winter when microbial activity in the lagoon is dormant in cold climates.

Most dairy waste lagoons are anaerobic in nature, and therefore nearly all of the nitrogen entering the lagoon is lost as volatilized ammonia due to nitrification and incomplete denitrification processes (Harper et al., 2000). An alternative to anaerobic conditions that would help reduce ammonia volatilization from lagoons is aeration. Aerated lagoons are oxygen-rich and promote the process of oxidation, oxidizing ammonia to nitrate, and increase the nitrification potential by converting ammonia to compounds like nitrous oxide (Flessa et al., 2002). Aerobic treatment of swine slurry has been shown to reduce odor and total slurry nitrogen by 56% after four days of aeration (Sneath et al., 1992). Even the intermittent use of aerators in swine lagoons has been shown to reduce total ammonia nitrogen, odor, and operating costs (Yang and Wang, 1999; Zhang and Zhu, 2005). Rarely, however, are dairy waste lagoons aerobic, as aeration is difficult to achieve in a dairy lagoon due to the high solids and protein content in the slurry (Cumby, 1987) and costly energy input. Rumburg et al. (2004) installed commercial aerators in a dairy lagoon and found no change in ammonia emissions, stating that the aerators failed to introduce enough oxygen into the lagoon to oxidize the ammonia. Due to the high oxygen demand of the nutrient rich solids in a lagoon, it is difficult to provide enough oxygen (1-2 mg/L) to achieve proper aeration in a waste lagoon (Cumby, 1987; Rumburg et al., 2004). The process of aeration can even be counter-productive, raising the pH of the lagoon, and actually inhibiting nitrifying bacteria and promoting ammonia volatilization (Zhang and Zhu, 2003). The best option to reduce ammonia volatilization from lagoons is to have a facultative or stratified lagoon, which has a top layer of aerobic activity to reduce ammonia and odor emission, and a bottom layer of anaerobic activity to promote microbial breakdown of solids and nutrients. Aerobic and anaerobic layering is achieved by mechanical circulation/aeration of the top layers of the lagoon, or can occur naturally in lagoons where solids are low, in secondary lagoons, or overflow lagoons with low solids content and nutrient load (Cumby, 1987). Lagoons that are partially aerated or circulated tended to cultivate nitrifying bacterial populations that reduced ammonia emissions by oxidizing ammonia to nitrite and nitrate (Sund et al., 2001). In order for this process to take place, the lagoon must be kept at a pH between 7 and 8 to maintain bacterial populations and minimize ammonia volatilization.

The rate of volatilization from the surface of a lagoon is influenced by environmental factors such as ambient temperature, relative humidity, surface wind velocity, and precipitation. To control these factors, the addition of a cover to the lagoon can reduce uncontrollable variables and capture unwanted emissions. A cover can be a floating plastic cover, a synthetic or natural cover of peat, straw, or polystyrene, or a natural cover formed by the presence of dry matter in the lagoon. When working properly, any of these covers can reduce nitrogen losses by 80-90% (Rotz, 2004), but any cracks in the cover will greatly reduce this efficiency. Misselbrook et al. (2005) found that the formation of a natural crust on the top of lagoons decreases ammonia emissions by up to 50%. The crust development occurs as a result of solids in the lagoon being carried to the surface by methane or carbon dioxide gas bubbles generated by microbial degradation of the organic matter in the lagoon. Evaporation at the surface of the lagoon promotes the drying of the solids and formation of the crust. The formation of a natural crust will occur when the lagoon has high solids content, the ambient air is dry, and there is little precipitation to break the crust.

Manure Piles and Composting

Of the total nitrogen entering manure storage/treatment as compost or manure stockpiles, 19 to 80% is lost through ammonia volatilization (Eghball et al., 1997; Amon et al., 2006), depending on storage treatment (Amon et al., 2006). The remaining nitrogen in the manure is converted to products of nitrification/denitrification (i.e. N_2O, N_2) or is immobilized. Some nitrous oxide losses occur during nitrification and incomplete denitrification, but these losses are usually less than 2% of the total nitrogen loss (Hao et al., 2001; Hao et al., 2004; Yamulki, 2006). Paillat et al. (2005) found that the ammonia flux in compost piles is related to the biodegradable nitrogen present and the nitrification and immobilization of ammonia, which depends on the C:N ratio, the carbon biodegradability, and microbes present in the pile. Less biodegradable carbon sources, like sawdust, were found to increase ammonia emissions; thus, the choice of added carbon source to a compost pile will impact the rate of ammonia emissions. Additionally, Paillat et al. (2005) noted that an increase in temperature of the compost pile increased ammonia volatilization from the pile. The amount of manure in the pile will directly affect the rapidity of temperature rise, and thus the ammonia volatilization. The greater the amount of manure in the pile, the faster the temperature will increase. After two days, all piles plateaued at the same temperature indicating that a maximum temperature had been reached in all compost piles. In another study, Liang et al. (2006) found that after four days, 90% of the total ammonia had volatilized from the compost pile, which they reported was correlated with the highest temperatures and the greatest amount of aeration of the compost pile. During this period, proper management of pile moisture and air circulation will determine the rate of temperature increase and subsequent ammonia volatilization. Composting BMPs that conserve nitrogen in the compost and reduce ammonia losses need to be developed.

During composting, nitrous oxide is emitted from nitrification and incomplete denitrification processes. Compared to ammonia emissions, the emission of nitrous oxide from compost and manure piles is very small, about 100 times less than that of ammonia (Paillat et al., 2005), or 0.8% of the total manure nitrogen (Flessa et al., 2002), but is still a problem due to its potential as a greenhouse gas. During the initial phases of composting, nitrous oxide emission is at a peak, likely due to aeration of previously anaerobic manure, which encourages denitrification and nitrous oxide emissions. Since nitrous oxide is produced during alternating aerobic and anaerobic conditions, maintaining anaerobic conditions in a manure pile will help decrease nitrous oxide emission (Monteny et al., 2006), but is impractical as it will increase emission of methane, odor, and ammonia, and possibly inhibit the composting process.

At temperatures above 40° C, Paillat et al. (2005) found that the production of nitrous oxide decreases significantly during the composting process. This is likely due to the prevention of nitrification at high temperatures. Therefore, maintaining a high temperature in the compost pile will decrease the emission of nitrous oxide. However, Paillat et al. (2005) also noted that an increase in temperature of the compost pile increased ammonia volatilization. It is possible that the decrease in nitrous oxide emissions during the high temperature phase of composting is due to the loss of the nitrogen as ammonia, whose emission increase with high temperatures.

Compost piles are comprised mainly of dried manure which can be lifted by the wind and carried to downwind locations. The concern with manure dust is that it can contain microbes and pathogens in manure which can be detrimental to human health. The composting process will render most pathogens inactive due to the high heat during the compost process (Pell, 1997). Keeping compost moist is essential for optimal composting and reduces the potential for dust production from composting sites.

Manure Application

Amon et al. (2006) found that the majority of ammonia emission occurred during application of slurry rather than during storage. They reported that the amount of ammonia volatilized during field application was directly correlated to the amount of ammonia that was retained during storage. Treatments with less ammonia emitted during storage, had more ammonia emitted during field application. Of the storage methods, liquid slurry had the highest ammonia volatilization during storage (81%), and manure solids the lowest (19%). It is important to note that storage options that reduce ammonia emissions, frequently only retain ammonia as nitrogen in manure, and after field application, it is often volatilized (Amon et al., 2006). Due to the volatile nature of ammonia, incorporation of slurry into the soil during or immediately after application is the most effective means of reducing ammonia emissions (Malgeryd, 1998; Sommer and Hutchings, 2001), and the deeper the incorporation, the less the emissions (Sommer and Hutchings, 2001). In a recent study of injection techniques, Rodhe et al. (2006) found that injection in closed slots resulted in no detectable ammonia emissions. However, due to increased nitrogen retention by the soil and low oxygen conditions at the injection site, injection may cause greater leaching and denitrification if application is not to meet crop nitrogen needs. The ideal solution to reduce nitrogen loss is to time manure application with the time of intense crop nitrogen demand so that nitrogen is captured by the plant rather than lost via volatilization or nitrate leaching (Van Horn et al., 1996; Rotz, 2004). Manure and soil should always be analyzed for nutrient content prior to application to cropland to match nutrient needs with application rates. Further research is necessary to determine the physical, biological and chemical processes involved in ammonia release under farm conditions. More specific information is necessary regarding ammonia emissions from various manure types, and farm-level emission data for ammonia model emission validation is also required. Multi-year emissions studies from land application would also be beneficial.

Gaseous emissions of nitrous oxide from manure application are generally small, between 1 and 4% of manure nitrogen applied and are generally unaffected by manure application method (Rotz, 2004). Rodhe et al. (2006) found that over 90% of observed nitrous oxide emissions occurred within the first 17 days after application and that emissions were greatest in injection treatments. Amon et al. (2006) found that nitrous oxide emissions after field application of dairy slurry ranged from 67 to 263 g N_2O-N ha^{-1} depending on the slurry treatment process (i.e. aeration, digestion, etc). They found that the addition of a straw cover to the slurry prior to application and separation of solids from the slurry retained more nitrogen (>20%) in the storage phase, which increased nitrous oxide emission during field application. Digested and aerated slurry had the least nitrous oxide.

CONCLUSION

Dairy and feedlot operations emit a variety of compounds to the atmosphere, such as ammonia, ammonium, and particulate matter, which may negatively impact the atmosphere, ecosystems, and human health. Fortunately, best management practices (BMPs) have been developed to help reduce those emissions and help animal operations decrease their negative impact. Some BMPs have been widely tested in laboratory and field conditions, while others are still in the early stages of research. The selection of

BMPs for an operation depends on a producers target pollutants and reduction goals. As noted in many of the BMPs sections, some BMPs may reduce the compound of choice, but can increase the emissions of others. The tradeoffs to BMP implementation must be considered when selecting BMPs to implement. For instance, by retaining ammonia in one area of the operation (i.e. the barn), it becomes more susceptible to emission later in the system (i.e. the lagoon or field application). If nitrogen is retained in manure, the possibility of nitrate leaching and runoff into ground and surface waters, respectively, may also increase. Additionally, some management practices that reduce ammonia emissions, such as decreasing lagoon pH or encouraging aerobic conditions in manure, can lead to an increase in hydrogen sulfide, odor, or nitrous oxide emissions. It must also be noted that the use of all the BMPs together is not feasible. A producer should select a few choice BMPs based on their economic standing, management practices, and reduction goals. Even with the proper use of BMPs, there will be some inevitable losses of gases from livestock operations. BMPs aid in mitigating losses and redirecting those inevitable losses to the least damaging pathways.

Table 2.1. Summary of nutrition related BMPs for ammonia (NH_3), nitrous oxide (N_2O), and particulate matter (PM) along with the cost effect of implementation and practicality of each BMP

		Emission[a]				
Nutrition BMPs	Animal Type	NH_3	N_2O	PM	Cost[b]	Practicality[c]
Reduce dietary N (protein) to match and animals needs	Dairy, Beef	--	--	--	-	++
Phase or group feeding	Dairy, Beef	--	-	-	0	++
Increase level of starch in diet	Dairy, Beef	-	NA	NA	+	+
Grind or pellet feedstuffs	Dairy, Beef	NA	NA	+	+	+
Provide bunkers for feed and minimize feed processing	Dairy, Beef	NA	NA	--	+	++
Increase animal health and efficiency (i.e. genetics, feed additives, clean environment etc.)	Dairy, Beef	--	-	0	+	++

[a] Major decrease= --; Minor decrease = -; No effect = 0; Major increase = ++; Minor increase = +;NA = No research available/Not applicable.

[b] Cost of implementation is: No difference in cost = 0; Low = -; High = +. Note: Cost is associated with implementation of the mentioned BMP and its effects only on the gases discussed.

[c] Practicality of implementation is: Not practical at all= --; Not practical = -; No difference = 0; Practical = +; Very practical = ++. Note: Practicality is a relative term and relates only to the specific BMP being discussed and its ease of implementation.

Table 2.2. Summary of animal housing related BMPs for ammonia (NH_3), nitrous oxide (N_2O), and particulate matter (PM) along with the cost effect of implementation and practicality of each BMP

		Emission[a]				
Animal Housing BMPs	Animal Type	NH_3	N_2O	PM	Cost[b]	Practicality[c]
Remove manure (flush/scrape) from barn alleyways frequently (6x/d)	Dairy	--	-	0	+	++
Utilize some type of floor surface modification to separate urine and feces	Dairy	--	0	0	+	++
Use sand bedding in freestalls	Dairy	--	+	-	-	+
Deep litter system	Dairy	-	++	NA	+	-
Provide adequate ventilation for enclosed barns	Dairy	--	NA	--	+	+
Reduce temperature in enclosed barns (20° C)	Dairy	-	NA	NA	+	+
Scrub exit air from enclosed barns (biofilters)	Dairy	--	NA	-	+	++

[a] Major decrease= --; Minor decrease = -; No effect = 0; Major increase = ++; Minor increase = +;NA = No research available/Not applicable.

[b] Cost of implementation is: No difference in cost = 0; Low = -; High = +. Note: Cost is associated with implementation of the mentioned BMP and its effects only on the gases discussed.

[c] Practicality of implementation is: Not practical at all= --; Not practical = -; No difference = 0; Practical = +; Very practical = ++. Note: Practicality is a relative term and relates only to the specific BMP being discussed and its ease of implementation.

Table 2.3. Summary of drylot corral related BMPs for ammonia (NH_3), nitrous oxide (N_2O), and particulate matter (PM) along with the cost effect of implementation and practicality of each BMP

		Emission[a]				
Drylot Corral BMPs	Animal Type	NH_3	N_2O	PM	Cost[b]	Practicality[c]
Scrape manure from pens frequently	Dairy, Beef	--	NA	--	+	++
Provide shade in pens and rotate feed and water locations	Dairy, Beef	-	NA	-	+	+
Correlate feeding times with crepuscular activity times	Dairy, Beef	NA	NA	--	0	+
Decrease soil surface pH below 6	Dairy, Beef	-	NA	NA	+	--
Provide bedding in drylot corrals	Dairy, Beef	-	+	+	+	-
Maintain a pen moisture level of 28%	Dairy, Beef	+	NA	-	+	-

[a] Major decrease= --; Minor decrease = -; No effect = 0; Major increase = ++; Minor increase = +;NA = No research available/Not applicable.

[b] Cost of implementation is: No difference in cost = 0; Low = -; High = +. Note: Cost is associated with implementation of the mentioned BMP and its effects only on the gases discussed.

[c] Practicality of implementation is: Not practical at all= --; Not practical = -; No difference = 0; Practical = +; Very practical = ++. Note: Practicality is a relative term and relates only to the specific BMP being discussed and its ease of implementation.

Table 2.4. Summary of waste management related BMPs for ammonia (NH_3), nitrous oxide (N_2O), and particulate matter (PM) along with the cost effect of implementation and practicality of each BMP

		Emission[a]				
Waste Management BMPs	Animal Type	NH_3	N_2O	PM	Cost[b]	Practicality[c]
Lagoon						
Anaerobic lagoon - no treatment	Dairy	+	-	NA	0	+
Acidification (pH<5) of anaerobic lagoon	Dairy	--	-	NA	+	--
Aeration of lagoon	Dairy	+	+	NA	+	--
Facultative lagoon (anaerobic bottom, aerobic top)	Dairy	-	NA	NA	+	++
Cover lagoon to collect/burn gases	Dairy	-	NA	NA	+	++
Decrease lagoon temperature	Dairy	-	NA	NA	+	-
Treat recycled lagoon water used to flush alleyways	Dairy	-	NA	NA	+	+
Maximize solid separation efficiency	Dairy	-	NA	NA	+	++
Composting						
Increase treatment temperature	Dairy, Beef	+	-	NA	+	-
Use a more biodegradable C source	Dairy, Beef	-	NA	NA	0	+
Manure Application						
Incorporate immediately after or during application	Dairy, Beef	--	+	NA	+	++
Time application to plant needs	Dairy, Beef	--	-	NA	0	++

[a] Major decrease= --; Minor decrease = -; No effect = 0; Major increase = ++; Minor increase = +;NA = No research available/Not applicable.

[b] Cost of implementation is: No difference in cost = 0; Low = -; High = +. Note: Cost is associated with implementation of the mentioned BMP and its effects only on the gases discussed.

[c] Practicality of implementation is: Not practical at all= --; Not practical = -; No difference = 0; Practical = +; Very practical = ++. Note: Practicality is a relative term and relates only to the specific BMP being discussed and its ease of implementation.

CHAPTER III

REVIEW: STRATEGIES TO REDUCE VOLATILE ORGANIC COMPOUNDS (VOC), ODOR, HYDROGEN SULFIDE, AND METHANE EMISSIONS FROM DAIRY AND FEEDLOT OPERATIONS

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ABSTRACT

Atmospheric emissions from animal agricultural operations have become a serious issue around the world. In the US, animal agriculture is a significant contributor to volatile organic compounds (VOC), odor, hydrogen sulfide, and methane. Due to its contribution to ozone depletion, smog, and decreased atmospheric visibility, VOC sources on farm are being more thoroughly researched, and emissions from fresh manure, ensiled feedstuffs and lagoons are being more accurately resolved. Odor, although widely recognized, is also recently being targeted for emission reduction, but with mixed success because some strategies that reduce odor can actually increase other compounds, and vise-versa. Hydrogen sulfide, a local nuisance and acute health hazard, is prevalent in waste management systems, and also has reduction challenges associated with companion compounds in waste systems (i.e. ammonia). Methane, emitted in large quantities from ruminant animals and waste systems, has received a lot of attention due to its contribution to global climate change as a greenhouse gas. Methane is prevalent in anaerobic waste systems such as lagoons and compost, but 75% of the total methane budget is contributed directly from ruminant fermentation, making reduction of methane emissions a challenge. Preceded by a summary of their sources, health and environmental impacts, a review of current methods available for mitigation of these pollutants is presented by area of nutrition, animal housing, drylot corrals, and waste management systems. The most feasible and economically viable solutions for emissions reduction have been presented as best management practices (BMPs) to reduce atmospheric emissions from dairy and beef feedlot operations. While many suggested BMPs will reduce emission of a select pollutant, they may increase emissions of another. Therefore, BMPs must be carefully chosen based on a producer's reduction goals as well as economic feasibility and ease of implementation. Even with the proper use of BMPs, there will be some inevitable losses of gases from livestock operations. BMPs aid in mitigating emissions and redirecting those inevitable losses to the least damaging pathways.

Keywords: Best management practices, Dairy, Feedlot, VOC, Odor, Hydrogen sulfide, Methane

INTRODUCTION

Dairy and beef feedlot operations emit a variety of emissions (volatile organic compounds (VOCs), odor, hydrogen sulfide, and methane) that can be directly or indirectly harmful to humans and natural ecosystems (Schiffman, 1998; Baron, 2006). Each atmospheric pollutant has its own source, mitigation techniques, and challenges. Whereas, some compounds are a regional problem (VOC, hydrogen sulfide, odor), others (methane) contribute to global climate changes (IPCC, 2006). Regional issues like odor, VOC and hydrogen sulfide are becoming an increasing concern due to the decreasing proximity of livestock operations and growing communities (Schiffman and Williams, 2005). Since dairy and feedlot operations are a significant contributor to odor, VOCs, hydrogen sulfide, and methane, they need to be targeted for reduction.

We conducted a literature review of relevant practices available to reduce emissions of VOC, hydrogen sulfide, odor and methane in viable and economically feasible ways. Preceded by a summary of their sources, environmental and human health impacts, techniques that could help reduce emissions from dairy and feedlot operations are discussed as best management practices (BMPs). Best management practices for reducing emissions from animal agriculture require the consideration of all pollutants and a defined reduction goal in order to be implemented into an operation. If properly selected and implemented, significant reductions in emissions could be achieved.

VOLATILE ORGANIC COMPOUNDS

Volatile organic compounds (VOC) are a group of hundreds of reactive compounds. The majority of VOC are emitted by vehicles, industrial processes and solvent usage (EPA, 2003), and biogenic sources which have been noted as significant contributors to VOC such as isoprene and monoterpenes (EPA, 2003). In the past few years, livestock sources are starting to be measured and quantified to evaluate their significance to anthropogenic VOC emissions. Some VOC associated with livestock odor are volatile fatty acids (VFA), mercaptans, phenols, amines, and sulfur compounds (e.g., dimethyl sulfide, hydrogen sulfide) (Miller and Varel, 2001; Filipy et al., 2006). While many VOC have been identified from livestock operations, the individual sources and concentrations are not well understood, nor are all of the direct health effects. A recent study by Mitloehner (2006) found that the majority of VOC emissions (ethanol and methanol) from dairies are emitted directly from the cow with a smaller amount emitted from fresh manure 2 to 3 hours after deposition; while Filipy et al. (2006) reported that the majority of emissions (ethanol, methanol, DMS) came from dairy freestall barns and lagoon inlets. Additionally, ensiled feedstuffs (silage) were identified as a significant source of VOC (Mitloehner, 2006). This would make barns and lagoons the major sources of VOC emissions from livestock operations, with drylot corrals also a significant contributor.

Environmental Impact

Volatile organic compounds are an atmospheric concern due to their chemical reactions in the atmosphere. Some VOC lead to global warming, while others contribute to ozone depletion, smog, and decreased atmospheric visibility (Finlayson-Pitts and Pitts, 2000).

The health effects of VOC are not well documented and currently are mostly associated with odor compounds and odor effects on human health (Shiffman et al., 1995).

ODOR

Odors are one of the most significant concerns for communities surrounding livestock operations, and consequently, are regulated as a nuisance in every state in the US (Miner, 1997). Odors are produced from a combination of gases including ammonia, hydrogen sulfide, VOC, volatile fatty acids (VFA), and products of reduced organic acids (i.e. acetic acid, isobutyric acid, etc.) (Zahn et al., 2001). The major source of odor production on a livestock operation is the anaerobic bacterial degradation of nutrients in manure (Miner, 1997). This occurs mainly in solid separation areas, manure piles, wastewater lagoons, drylot corrals with a deep manure pack, dairy barns, and other manure-laden areas. The intensity and duration of odor will depend on the season, wind speed, wind direction, and other factors. An increase in seasonal temperature tends to increase odors by activating and catalyzing bacterial reactions in the manure (Moller et al., 2004). Additionally, the spring tends to bring more odors from lagoons due to reactivation of dormant bacterial populations with warmer temperatures.

Human Health Impact

The impact of odor on local communities and neighbors who reside near livestock operations is variable. The effects of odor on human health have been widely explored, and adverse heath effects have been documented (Schiffman, 1998; Schiffman et al., 1995, 2000). Schiffman et al. (2000) noted that health complaints associated with odorous air pollutants has increased dramatically with the presence of large livestock operations near communities. Authors reported that the most commonly reported health complaints related to odor included eye, nose and throat irritation, headache, nausea, cough, congestion, labored breathing, increased asthma, drowsiness, and altered mood. However, there is substantial variation in human response, partly due to perceived odor and cognitive expectations about the effects an odor "should" have (Schiffman et al., 1995). It has been found that a negative mood, stress, and environmental worry may lead to biochemical and physiological effects with subsequent health outcomes (Schiffman, 1998). Physiologically, an odor works by stimulating and activating cranial and oral cavity nerve receptors, which send signals to the brain about the odor eliciting a physiological response. The response is based on the person's perception of the odor and their prior exposure (Schiffman, 1998). People who work at livestock operations become desensitized to odors over time and find them less offensive than someone who is periodically exposed to odors. People that are periodically exposed to odors can actually become more sensitized to the odor and detect it at lower thresholds (Schiffman, 1998). This makes regulation of odor thresholds, along with issues in measuring odors, very difficult.

HYDROGEN SULFIDE

Hydrogen sulfide is produced on livestock operations from the anaerobic decomposition of sulfur by sulfur-reducing bacteria. Hydrogen sulfide emissions are primarily associated with manure handling systems such as lagoons, wet manure piles, and solid separation areas. In general, hydrogen sulfide is primarily emitted from dairy waste lagoons.

Human Health Impact

Hydrogen sulfide odor is detectable at low levels (0.5 ppb), making it a primary contributor to odor complaints. It also has detrimental human health effects at high levels. Merchant et al. (2003) report that at 2 ppm, hydrogen sulfide can cause headache, nausea, eye and throat irritation, airway resistance, and reduced aerobic metabolism. At concentrations greater than 10 ppm, oxygen uptake is decreased and blood lactate increased. Although low doses are not serious, prolonged exposure can lead to neuropsychological abnormalities, including impaired balance, visual field performance, color discrimination, hearing, memory, mood, and intellectual function (Merchant et al., 2003). At higher concentrations (greater than 100 ppm), hydrogen sulfide exposure can lead to loss of consciousness, pulmonary edema, coma, and death (Merchant et al., 2003). Hydrogen sulfide can build up in closed manure handling tanks and at concentrations greater than 100 ppm, causing rapid loss of consciousness and asphyxiation, and is one of the leading causes of death on livestock operations (Merchant et al., 2003). Most exposure, however, is below these extreme levels.

METHANE

Globally, the EPA (2006) estimates that livestock contributes to 28% of the total US methane budget. The main source of methane production from livestock is ruminant enteric fermentation in beef and dairy cattle. Enteric fermentation is the microbial digestion of cellulose material in the rumen, which is then released as methane gas by eructation (belching). This process contributes to about 75% of total livestock methane emission (EPA, 2006). The other 25% of methane emissions from livestock is produced from anaerobic decomposition of organic matter in manure and anaerobic waste lagoons. EPA (2006) reports that since 1995, methane emissions from livestock have decreased 5% due to a reduction in cattle numbers in the US and improved feed quality. However, livestock are still a significant source of methane, and further reductions would aid in decreasing the total greenhouse gas budget.

Environmental Impact

Due to its thermal absorption properties, and increasing concentration in the atmosphere, methane gas is one of the top greenhouse gases (others: carbon dioxide and nitrous oxide) responsible for global climate change. Due to its extensive sources and relatively long lifetime (10 years), methane is being produced and stored in the atmosphere at a much faster rate than it can be consumed by soil and chemical processes (Godish, 2004). Since cattle operations contribute such a significant portion of the global methane budget (28%; EPA, 2006), they are a main target for methane reduction.

EMISSION REDUCTION STRATEGIES

Animal Nutrition

A summary of BMPs discussed for nutritional reduction of VOC, odor, hydrogen sulfide, and methane emissions is presented in Table 3.1. The relative reduction potential is illustrated along with cost of implementation and practicality of the BMP. The effects of the BMP to VOC, odor, hydrogen sulfide, and methane are also included to show the connectivity of mitigation techniques on the entire system rather than just one species.

Following is a review of nutritional practices that could reduce emissions of VOC, odor, hydrogen sulfide, and methane.

Since 75% of the total livestock methane budget is from ruminant eructation (EPA, 2006), nutritional strategies that reduce enteric methane production will greatly reduce the methane produced on farm. Johnson and Johnson (1995) conducted a comprehensive analysis of methane emissions from cattle and found a variety of nutritional factors that influenced the production of methane from cattle. They reported that methane can be reduced by increasing the level of starch or rapidly fermentable carbohydrates in the diet, which impacts the ruminal pH and microbial population, both of which regulate methane production. They also reported that an increase in feed intake will increase methane production; grinding and pelleting of forages can decrease methane production; long-chain polyunsaturated fatty acids decrease methanogenesis; and ionophore additions (e.g., monensin) decrease methane loss from enteric fermentation. They concluded that the best way to mitigate cattle methane production is by enhancing the efficiency of feed energy use. Since methane emission is the byproduct of incomplete digestion, higher quality diets will allow animals to better digest their feed, decreasing methane production potential. Monteny et al. (2006) reported the three most important factors in enteric fermentation are the rate of organic matter fermentation, type of volatile fatty acids produced, and the efficiency of microbial biosynthesis. When the rate of organic matter fermentation increases, the rumen pH will drop and shift volatile fatty acid production towards more propionate, which will stop free hydrogen from being used to produce methane. Additionally, an increase in the level of starch or rapidly fermentable carbohydrates will enhance propionate production, thus lowering methane production

(Monteny et al., 2006). The use of ionophores has also been shown to decrease enteric methane production by up to 30% for the first 2 to 4 weeks of supplementation (Guan et al., 2006).

Ruminant enteric fermentation of feed is also a source of VOC production. When animals eructate, it releases VOC (ethanol and methanol) produced in the rumen from the fermentation of feed. Mitloehner (as reported in Rovner, 2006) found that lactating cows release as much as six times more alcohol VOC than dry cows due to their higher metabolic rate and diet. The direct emission of VOC from cattle needs additional research and quantification before any reduction practices can be proposed.

Mitloehner (as reported in Rovner, 2006) reported that fermented feed, such as silage, is also a significant source of VOC production on dairies. Different types of silage will have different VOC emission potentials, but silage types that are low in sugar will have the least VOC emissions due to lower fermentation rates. Overall, he reported that VOC emissions from fermenting feed can be an order of magnitude greater than emissions from fresh animal waste on a mass basis.

With the increasing demand for alternative fuel sources, ethanol production from corn has become widespread resulting in a byproduct called distillers grains. Gralapp et al. (2002) looked at the effect of dietary distillers grains on swine manure odor characteristics. They found a trend of increased odor, but recommended that further research be conducted to evaluate this impact. Trials with cattle also need to be conducted in this field to quantify the significance of distillers grains on cattle manure odor. Since manure odor is a product of the anaerobic breakdown of undigested feed components, it is possible that ingredient selection may serve as a means for promoting or preventing certain odorants in manure (Gralapp et al., 2002). By matching an animal's feed intake to its requirements, the amount of nitrogen and sulfur containing nutrients in the diet can be minimized, reducing the output of these nutrients that lead to odor-causing compounds like ammonia, hydrogen sulfide, and other odorants.

While no data or significant emissions have been reported for hydrogen sulfide in nutritional trials, similar to crude protein and nitrogen excretion (Cole et al., 2005), a reduction in sulfur intake will decrease the excretion of sulfur compounds (NRC, 2001), minimizing the amount of sulfur in the waste handling stream. Gralapp et al. (2002) found that in swine diets, a higher sulfur content in the diet led to increased sulfur excretion and production of malodorous sulfur-containing compounds. Stevens et al. (1993) reported that dairy cattle diets high in protein and sulfur lead to an increase in the excretion of sulfur compounds and subsequent hydrogen sulfide and dimethyl sulfide (DMS) emission from the manure slurry, a significant odorant from dairy operations (Filipy et al., 2006).

Animal Housing

A summary of BMPs discussed for reduction of VOC, odor, hydrogen sulfide, and methane emissions from animal housing is presented in Table 3.2. The relative reduction potential is illustrated along with cost of implementation and practicality of the BMP. The affects of the BMP to VOC, odor, hydrogen sulfide, and methane are also included to show the connectivity of mitigation techniques on the entire system rather than just one species. Following is a review of practices that could reduce emissions of VOC, odor, hydrogen sulfide, and methane from animal housing facilities.

The direct emission of methane from manure deposited in barns is very small (less than 0.4 kg/d) (Zhang et al., 2005), while ruminant enteric fermentation in barns produces 80% of the total methane emissions (Monteny et al., 2001; Hilhorst et al., 2002). For dairy cows housed in enclosed barns, the most effective way to reduce methane is with the use of bio-filters located at exhaust air outlets. Bio-filters can be seeded with methanotrophic bacteria that will oxidize methane to carbon dioxide, reducing the methane emitted to the atmosphere from barns. The addition of a bio-filter or scrubber to the exhaust air will trap methane along with other compounds (odor, hydrogen sulfide, ammonia) and decrease emissions released to outside ambient air (Miner, 1997; Melse and Ogink, 2005). Melse and Ogink (2005) reported that the use of acid scrubbers and biotrickling filters removed odor from the exit air or swine and poultry barns with a removal efficiency of 27 and 43%, respectively. Koziel (as reported in Rovner, 2006) suggests one method of biofiltration that filters exhaust air through a large bed of moist woodchips covered in bacteria, which thrive on odorous gases, essentially cleaning the exhaust air of odor and dust. This system is inexpensive and requires only the application of water to keep the woodchips moist. More research needs to be done in this area to find the best and most effective biofilters available for this purpose.

Filipy et al. (2006) measured VOC emission from a freestall dairy barn and found that methanol and ethanol were the two primary alcohol VOCs emitted from fresh manure. They also reported emission of DMS from the manure, a main component in odorous compounds. Miller and Varel (2001) reported that ethanol from feedlot manure accounted for 95% of total alcohol emissions from manure, flowed by propanol (3%) and butanol (1%). Mitloehner (2006) also reported that the majority of VOC emissions occurred from fresh manure within a few hours after deposition to the barn floor. Mitloehner (2006) suggests that by increasing the flushing rate in flush dairy barns to every two hours, VOC emission can be reduced by removing the manure and exposing it to water as quickly as possible, suspending the alcohols in solution and preventing volatilization.

Drylot Corrals

A summary of BMPs discussed for reduction of VOC, odor, hydrogen sulfide, and methane emissions from drylot corrals is presented in Table 3.3. The relative reduction potential is illustrated along with cost of implementation and practicality of the BMP. The effects of the BMP to VOC, odor, hydrogen sulfide, and methane are also included to show the connectivity of mitigation techniques on the entire system rather than just one species. Following is a review of practices that could reduce emissions of VOC, odor, hydrogen sulfide, and methane from drylot corrals.

The volatilization potential of VOC from drylot surfaces is very high. Due to the rapid rate of VOC emission from fresh excreta (a few hours) and the infrequency of manure harvest from pen surfaces (one week to one year), there is usually sufficient time for total VOC volatilization to take place from drylot corral surfaces. Miller and Varel (2001) reported that ethanol and VFA production from feedlot manure was very high, and that the emission of VFA is directly linked to odor production from drylot surfaces. The rate of odor production can be reduced if the feces and urine are separated from one another or if the manure is kept aerobic, which will reduce the production of odorous compounds. The use of bedding, such as straw, can help separate the urine and feces portions of the excreta, reducing their mixing potential (Miner, 1997). It can also provide oxygen to the excreta, as long as a sufficient amount of bedding is available to let oxygen permeate the bedding mass (Miner, 1997).

Usually, methane production directly from drylot surfaces is insignificant. The primary source of methane production from drylots would be from enteric fermentation and subsequent eructation and flatulence, which releases methane directly from cattle in the drylot. This direct animal source contributes to 75% of the total methane emissions from a livestock operation (EPA, 2006). Of the total amount of methane contributed by livestock through enteric fermentation, beef cattle contribute 71% and dairy cattle 24% to the total agricultural methane budget (EPA, 2006). Beef cattle contribute more to the budget because total beef cattle numbers are greater than dairy cattle.

If drylots are allowed to accumulate moisture and a deep manure pack, they will become anaerobic and begin to emit methane, hydrogen sulfide and odor from bacterial degradation of organic matter in the manure. The moisture content of the pen surface has been directly linked to the production of odor (Miller and Berry, 2005). With increasing moisture content, the production of odorous compounds is maximized. A low moisture level will decrease the production of volatile fatty acids and other odorous compounds, but will greatly increase the production of dust. A surface moisture level of 28% has been suggested to balance odor and dust (Miller and Berry, 2005). The frequent removal of manure from the pen surface would help decrease this potential.

Waste Management Systems

A summary of BMPs discussed for reduction of VOC, odor, hydrogen sulfide, and methane emissions from waste management systems is presented in Table 3.4. The relative reduction potential is illustrated along with cost of implementation and practicality of the BMP. The effects of the BMP to VOC, odor, hydrogen sulfide, and methane are also included to show the connectivity of mitigation techniques on the entire system rather than just one species.

Animal waste is a significant source of odor, hydrogen sulfide, VOC, and methane production on livestock operations. Immediately after excretion, volatile materials in manure begin to volatilize, and malodor is detectable. A variety of waste management technologies have been proposed to help reduce odors and methane from waste processing including covered anaerobic digesters, solid separation, bio-filters, nitrification-denitrification systems, and others (Schiffman and Williams, 2005). Following is a review of practices that could reduce emissions of VOC, odor, hydrogen sulfide, and methane from waste management systems.

Lagoons and Slurry Storage

Prior to entering a lagoon, the separation of the solid and liquid portion of the influent has been shown to help reduce odors in lagoons by removing the manure solids which contain about 40% of odor generating compounds (Zhang and Zhu, 2003). The solids (organic matter) not removed with solid separation enter the lagoon and promote an odor generating environment. Therefore, maintaining optimal efficiency and function of a solid separation system will help reduce odor in the lagoon.

The anaerobic degradation of organic matter in dairy waste lagoons leads to the formation of intermediate volatile fatty acids (VFA) (acetate, propionate, and butyrate), which are some of the most prominent odorous species (Miller and Varel, 2001). Acetate, the most prevalent VFA (Moller et al., 2004), is then further degraded to carbon dioxide and methane by methanogens. Moller at al. (2004) found that 60% of the VFA in cattle manure was acetic acid (acetate), which contributed to an in crease in methane emissions. Zhang and Zhu (2003) found that aeration of swine lagoons reduced the total solids content of a waste lagoon and the VFA concentration. After three months of aeration, they reported that the VFA removal efficiency of the lagoon was 98%, with newly added manure being consumed within 10 hours of aeration. Zhang and Zhu (2003) also verified that the dissolved oxygen content of lagoons at deeper depths delayed the appearance of sulfur gases, such as hydrogen sulfide, which is an odor contributing gas. Surface aeration, which can be either mechanical or chemical, will also help decrease the emission of hydrogen sulfide from the lagoon. Miner (1997) pointed out that while aeration can reduce odor, the operational costs of aerating a livestock lagoon has made the process very unattractive to producers. Xue and Chen (1999) looked at an alternative aeration technique that applied hydrogen peroxide to a dairy lagoon surface to oxidize hydrogen sulfide at the surface. They found that the hydrogen peroxide was successful in oxidizing hydrogen sulfide to elemental sulfur of sulfate, but that reductions were only seen for 10 days before reapplication was necessary. Therefore, this may not be a practical method. Miner (1997) suggests having an anaerobic lagoon and installing a cover which will help reduce odor by decreasing the ventilation rate of the lagoon and, hence, the rate of odor emissions (Miner, 1997). The cover can be ridged or permeable, but should be managed well and be free of tears or cracks which will negate the mitigation of odor. The addition of a cover to the lagoon will also aid in capturing hydrogen sulfide and methane gases before they are emitted into the atmosphere. The controlled anaerobic digestion of slurry has been shown to reduce methane emissions by capturing the biogas produced and using it as an alternative to fossil fuel (Hilhorst et al., 2002). Biogas production from anaerobic digesters is not only a feasible way to trap methane and other gases, but combined with generation of power, is the most feasible and possibly most cost effective method of methane reduction from manure (Monteny et al., 2006). The only caveat is that if the cover is not sealed and maintained properly, the emission of methane can be higher than if no cover was present. Hilhorst et al. (2002) reported that in a digester, the production of biogas can be 100 times higher than with conventional storage, and a gas leakage of 1% equals the emission of methane from conventional manure storage. If not captured and converted to energy, the burning/flaring of methane gas from digesters or pits is also an effective way to reduce methane emissions (Monteny et al., 2006). It can then be burned off with other captured gases (i.e. methane, ammonia).

Biological methods to control hydrogen sulfide emissions, such as purple sulfur bacteria, have been proposed, but are still under examination. Purple sulfur bacteria (PSB) are photosynthetic, anaerobic bacteria that grow in the presence of carbon dioxide (carbon source), nitrate (nitrogen source), and hydrogen sulfide, which is utilized as an electron donor for photosynthesis (White, 2000). Purple sulfur bacteria oxidize the hydrogen sulfide in the lagoon for photosynthesis and produce elemental sulfur or sulfate as a photosynthetic by-product (Sund et al., 2001), both of which are less odorous than hydrogen sulfide. Since PSB are photosynthetic, the use of a solid separator can aid in light penetration and the proliferation of PSB in a lagoon. Additionally, since PSB are photosynthetic facultative organisms, they will be in varying concentrations at different depths in the lagoon. Some species of PSB can tolerate mild levels of oxygen, while others can tolerate none. Thus, a lagoon can have different species of PSB depending on its oxygen level. Sund et al. (2001) found that sulfate reduction via sulfate reducing bacteria, was the dominant nutrient conversion process at greater depths where light and oxygen are low. The presence of high levels of oxygen in the lagoon water is actually detrimental for PSB production and will lead to population stratification in the lagoon. The presence of a circulator in the lagoon aids in mixing the lagoon for maximum sunlight exposure for all depths of the lagoon. The circulator also allows PSB at upper layers of the lagoon to contribute their nutrient product to lower layers, and visa-versa for sulfate reducing bacteria. The temperature range for proliferation is between 18 and 30 C, and the pH range is 7.0 to 8.5, with optimum at 26.5 C, and pH 7.5 (Freedman et al., 1983). At a pH below 8.0, a significant fraction of the hydrogen sulfide is present in the un-ionized or dissolved gas form.

An additional method of methane and odorous VFA reduction is lowering the pH of the slurry with additives such as lactic acid (Monteny et al., 2006) or alum. Methane production is at an optimum around pH 7, and inhibited at pH below 6 (Miller and Varel, 2001). VFA production from cattle slurry is inhibited at a pH below 4.5 (Miller and Varel, 2001). In order to maximize the benefit of a reduction in lagoon pH, optimum pH levels of ammonia and nitrous oxide should also be considered. In order to decrease the emission of all three gases significantly, the pH of the lagoon would need to be lowered to pH 4.5 (Miller and Varel, 2001; Hilhorst et al., 2002). This is possible in a small scale waste containment situation, but becomes costly and impractical on a large scale basis. Another side effect is that reducing the pH of a lagoon will increase hydrogen sulfide emissions. Hydrogen sulfide emission are lowest at a pH above 7.5 (Freedman et al., 1983), and highest at a pH under 6.5.

In addition to pH, temperature can be used to control emissions of some gases. Moller et al. (2004) reported greater losses of methane at higher temperatures for cattle manure, especially during long term anaerobic storage. An increase in methane emission due to increasing temperatures has been reported in a variety of studies (Hill et al., 2001; Hilhorst et al., 2002; Moteny et al., 2006). Hill et al. (2001) demonstrated a linear increase in methane production with increasing temperature between 10° and 20° C in anaerobic digesters. Hilhorst et al. (2002) suggested using this temperature control to decrease the emission of methane from slurry by cooling the slurry. They reported a 66% decrease in methane emissions from pig slurry cooled by 7° C by transferring it from indoor tanks to an outdoor lagoon. Similar results were found for cattle slurry stored outdoors, where a 1 to 2° C decrease in temperature resulted in a 5 to 10% reduction in methane emissions.

Unlike odor and methane, long term dairy waste storage lagoons have been shown by Mitloehner (as reported in Rovner, 2006) to be a negligible source of VOC emission. This is due to the rapid rate of volatilization of VOC that occurs in other areas of the livestock operation, like the barns. Filipy et al. (2006) reported that while lagoons emitted VOC such as ethanol and DMS, but that freestalls were a much more significant source of these pollutants.

Composting and Manure Storage

Livestock manure is a significant source of methane, especially during storage due to anaerobic bacterial degradation of organic matter. The production of methane from animal waste is affected by several factors including storage time, manure characteristics, methanogenic bacterial populations, daily and seasonal temperature changes, and oxygen and carbon availability (IPPC, 1996; Hao et al., 2001; Hao et al., 2004). Hao et al. (2001, 2004) reported that methane production is highest at the bottom and center of a manure or compost pile where anaerobic conditions exist, and is oxidized as it reaches the top aerobic section of the pile and emitted as carbon dioxide. For this reason, Hao et al. (2004) found that carbon losses as methane from compost represented less than 6% of the total carbon loss from the pile. Hao et al. (2001) reported that methane was 7.9% of the total gaseous carbon loss, and Yamulki (2006) reported only 0.06%. Although methane had a seeming small contribution to total carbon loss, its greenhouse gas effect is far grater than carbon dioxide since methane is 21 times more powerful as a greenhouse gas (IPCC, 2006), resulting in the largest total greenhouse gas emission in terms of CO_2 equivalents. Therefore, any reduction could be quite significant. Yamulki (2006) found that the addition of straw to compost piles reduced methane emissions by 45% from conventional cattle manure. The author postulates that this was due to increased dry matter and aeration of the pile from the straw addition. The amount of straw used in the composting process directly affected the amount of greenhouse gas emitted. Aeration of the pile with active aeration or turning will aid in oxygenating the pile and helping to decrease methane emissions.

Manure Application

Methane emissions from field application of manure tends to be small (Amon et al., 2006; Rodhe et al., 2006), ranging from 1.3 to 22.2 g CH_4 m^{-3} slurry, and usually occurs at anaerobic microsites. The majority of methane emission after manure slurry application on grasslands appears to be short-lived and may occur within two days after application (Chadwick et al., 2000; Rodhe et al., 2006). Four years after manure application had stopped in Mead, Nebraska, Ginting et al. (2003) found no difference between manured and non-manured treatments, or were able to measure methane from the soil due to the limited emissions. Other researchers have observed methane production after surface application or injection (Flessa and Beese, 2000). Rodhe et al. (2006) suggested that the methane emission from manure application was possibly due to the injection of methane-producing bacteria into the soil.

CONCLUSION

Dairy and beef feedlot operations emit a variety of compounds to the atmosphere, such as VOCs, odor, hydrogen sulfide, and methane, which may negatively impact communities, the atmosphere, and human health. Fortunately, best management practices (BMPs) have been developed to help reduce these emissions and help animal operations decrease their negative impact. The selection of BMPs for an operation depends on a producers target pollutants and reduction goals. As noted in some of the sections addressing BMPs above, some BMPs will reduce the compound of choice, but can increase the emissions of others. The tradeoffs of BMP implementation must be considered when selecting BMPs.

Additionally, it must be noted that the use of all the BMPs together is not feasible. A producer should select a few choice BMPs based on their economic standing, management practices, and reduction goals. Even with the proper use of BMPs, there will be some inevitable losses of gases from livestock operations. BMPs aid in mitigating losses and redirecting those inevitable losses to the least damaging pathways.

Table 3.1. Summary of animal nutrition related BMPs for hydrogen sulfide (H2S), volatile organic compounds (VOC), odor, and methane (CH4), along with the cost effectiveness of implementation and practicality of each BMP

		Emission[a]					
Nutrition BMPs	Animal Type	H_2S	VOC	Odor	CH_4	Cost[b]	Practicality[c]
Reduce dietary N (protein) and S to match and animals needs	Dairy, Beef	-	-	-	NA	-	++
Phase or group feeding	Dairy, Beef	-	NA	-	0	+	++
Increase level of starch in diet	Dairy, Beef	NA	NA	NA	--	+	+
Grind or pellet feedstuffs	Dairy, Beef	NA	NA	NA	--	+	+
Use ionophores in feed	Dairy, Beef	NA	NA	NA	--	+	-
Properly manage ensiled feedstuffs	Dairy, Beef	NA	--	-	NA	0	+
Increase animal health and efficiency (i.e. genetics, feed additives, clean environment etc.)	Dairy, Beef	-	NA	-	-	0	++

[a] Major decrease= --; Minor decrease = -; No effect = 0; Major increase = ++; Minor increase = +;NA = No research available/Not applicable.

[b] Cost of implementation is: No difference in cost = 0; Low = -; High = +. Note: Cost is associated with implementation of the mentioned BMP and its effects only on the gases discussed.

[c] Practicality of implementation is: Not practical at all= --; Not practical = -; No difference = 0; Practical = +; Very practical = ++. Note: Practicality is a relative term and relates only to the specific BMP being discussed and its ease of implementation.

Table 3.2. Summary of barn related BMPs for hydrogen sulfide (H_2S), volatile organic compounds (VOC), odor, and methane (CH_4), along with the cost effectiveness of implementation and practicality of each BMP

		Emission[a]					
Barn BMPs	Animal Type	H_2S	VOC	Odor	CH_4	Cost[b]	Practicaltiy[c]
Remove manure (flush/scrape) from barn alleyways frequently (6x/d)	Dairy	-	--	-	NA	+	++
Utilize some type of floor surface modification to separate urine and feces	Dairy	NA	NA	-	NA	+	++
Use sand bedding in freestalls	Dairy	NA	NA	-	NA	-	+
Provide adequate ventilation for enclosed barns	Dairy	-	-	--	-	+	+
Reduce temperature in enclosed barns (20° C)	Dairy	NA	-	-	-	+	+
Scrub exit air from enclosed barns (biofilters)	Dairy	-	-	-	--	+	++

[a] Major decrease= --; Minor decrease = -; No effect = 0; Major increase = ++; Minor increase = +;NA = No research available/Not applicable.

[b] Cost of implementation is: No difference in cost = 0; Low = -; High = +. Note: Cost is associated with implementation of the mentioned BMP and its effects only on the gases discussed.

[c] Practicality of implementation is: Not practical at all= --; Not practical = -; No difference = 0; Practical = +; Very practical = ++. Note: Practicality is a relative term and relates only to the specific BMP being discussed and its ease of implementation.

Table 3.3. Summary of drylot corral related BMPs for hydrogen sulfide (H_2S), volatile organic compounds (VOC), odor, and methane (CH_4), along with the cost effectiveness of implementation and practicality of each BMP

		Emission[a]					
Drylot Corral BMPs	Animal Type	H_2S	VOC	Odor	CH_4	Cost[b]	Practicality[c]
Scrape manure from pens frequently	Dairy, Beef	-	-	--	-	+	++
Provide shade in pens and rotate feed and water locations	Dairy, Beef	NA	NA	-	NA	+	+
Correlate feeding times with crepuscular activity times	Dairy, Beef	NA	NA	-	NA	0	+
Decrease soil surface pH below 6	Dairy, Beef	+	NA	-	-	+	--
Provide bedding in drylot	Dairy, Beef	NA	-	-	-	+	-
Maintain a pen moisture level of 28%	Dairy, Beef	NA	NA	-	NA	+	-

[a] Major decrease= --; Minor decrease = -; No effect = 0; Major increase = ++; Minor increase = +;NA = No research available/Not applicable.

[b] Cost of implementation is: No difference in cost = 0; Low = -; High = +. Note: Cost is associated with implementation of the mentioned BMP and its effects only on the gases discussed.

[c] Practicality of implementation is: Not practical at all= --; Not practical = -; No difference = 0; Practical = +; Very practical = ++. Note: Practicality is a relative term and relates only to the specific BMP being discussed and its ease of implementation.

Table 3.4. Summary of waste management related BMPs for hydrogen sulfide (H_2S), volatile organic compounds (VOC), odor, and methane (CH_4), along with the cost effectiveness of implementation and practicality of each BMP

		Emission[a]					
Waste Management BMPs	Animal Type	H_2S	VOC	Odor	CH_4	Cost[b]	Practicality[c]
Lagoon							
Anaerobic lagoon - no treatment	Dairy	++	+	++	+	0	+
Acidification (pH<4.5) of anaerobic lagoon	Dairy	++	NA	--	--	+	--
Aeration of lagoon	Dairy	-	-	-	-	+	-
Facultative lagoon (anaerobic bottom, aerobic top)	Dairy	-	NA	-	-	+	++
Cover lagoon to collect/burn gases	Dairy	-	-	--	--	+	++
Decrease lagoon temperature	Dairy	-	NA	-	--	+	-
Treat recycled lagoon water used to flush alleyways	Dairy		NA		NA	+	+
Maximize solid separation efficiency	Dairy	-	NA	--	-	+	++
Composting							
Aerate compost piles	Dairy, Beef	NA	NA	-	-	+	+

[a] Major decrease= --; Minor decrease = -; No effect = 0; Major increase = ++; Minor increase = +;NA = No research available/Not applicable.

[b] Cost of implementation is: No difference in cost = 0; Low = -; High = +. Note: Cost is associated with implementation the mentioned BMP and its effects only on the gases discussed.

[c] Practicality of implementation is: Not practical at all= --; Not practical = -; No difference = 0; Practical = +; Very practical = ++. Note: Practicality is a relative term and relates only to the specific BMP being discussed and its ease of implementation.

CHAPTER IV

A PROFILE SAMPLING METHODOLOGY FOR MEASURING GASEOUS EMISSIONS FROM DAIRIES

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ABSTRACT

Emissions from livestock operations are of growing concern. While point source emissions have been well characterized, emissions from the whole farm have not. Currently, no reported system has been developed for livestock operations to measure whole plume concentrations at heights over 10 m; however, most gases are still present at heights above 10 m. We present a whole farm measurement system that quantifies concentration and meteorological profiles downwind of livestock operations using helium blimps to sample gases and particulates at various heights (up to 100 m) to characterize the horizontal and vertical extent of emission plumes. The system is designed to measure trace gases (carbon dioxide, methane, and nitrous oxide) using syringe pumps, and nitrogen species (nitric acid, ammonia, and ammonium) using specially designed filter packs attached to the tether lines of the blimps. The objective of this study was to demonstrate the validity of the system under field conditions, test the efficiency of sampling equipment in the lab and field, and show gaseous profiles obtained from measurement at a dairy. Results showed that filter packs had good recovery for ammonia (97.7%) and nitric acid (97.5%) and compared well against denuders (difference: 21%, nitric acid, 17% ammonia), and that the system worked efficiently when operated under field conditions. Additionally, results from a field trial demonstrated that gaseous profiles from a dairy varied with species measured as well as height and sampling location. These results can be used to characterize emission plumes from livestock operations and provide a better understanding of the behavior of gaseous emissions from heterogeneous livestock emission plumes.

Keywords: Dairy emissions, Greenhouse gases, Ammonia, Profile sampling

INTRODUCTION

Livestock operations are known to be major contributors of atmospheric gaseous and particulate pollutants (ammonia, ammonium, carbon dioxide, methane, and nitrous oxide), but the magnitude and profile of these emissions is poorly known. Various methodologies (i.e. flux chambers, remote sensing equipment, and models) have been employed to quantify emissions from livestock operations, but each has shortcomings when trying to characterize an emission plume from a whole operation. For example, flux chambers have been used in a variety of studies to characterize emissions from livestock operations (Gholson et al., 1991; Eklund, 1992; Aneja et al., 2000; Sommer et al., 2006) by measuring surface emission flux, but are limited in their ability to obtain a representative sample from farming systems due to limitations associated with long sample times and a small sampling surface area (Eklund, 1992).

To measure gas and particulate concentrations in the lower atmosphere above, and downstream of, larger farm systems, remote sensing techniques have been developed and employed in the field. These include open-path Fourier transform infrared (FTIR) spectroscopy (Shores et al., 2005), differential optical absorption spectroscopy (DOAS) (Rumburg et al., 2004), and tunable diode laser systems (Laubach and Kelliher, 2005). These systems have been used to estimate emissions from large area sources such as lagoons, drylots, and fields with high time and temporal resolution and good accuracy. However, their main limitation is that they must have an unobstructed path over the emission source, making measurements for an entire farm difficult. Additionally, the equipment is expensive and requires a trained technician to operate it efficiently. To limit the need for whole plume measurement systems and high field operation costs, models have been developed to try to characterize both nitrogen and greenhouse gas species emissions qualitatively and quantitatively. Most models use data collected from field trials to create estimates of emissions from a livestock operation based on user input about system and management techniques (Pinder et al., 2004a; Flesch et al., 2005). Some models work on characterizing parts of an operation such as composting (Liang et al., 2004), animal housing (Quinn et al., 2001; Vranken et al., 2004), animal nutrition (IPCC, 2006), or animal excreta (Kebreab et al., 2004), while others aim at characterizing the entire system (Kohn et al., 1997; Pinder et al., 2004b). The major limitations of models are that most only predict the emissions of one pollutant, most model output is for emission values no higher than 10 m, and no current model is able to integrate all of the management variations that influence emissions, nor do they account for meteorological variables, both of which greatly affect emissions and resulting concentration profiles above and downwind of a farm (Robarge et al., 2002).

The limiting factor of the methods discussed above is that they generally do not provide measurements for an entire livestock operation, but rather measure pieces of the whole system. In order to characterize emissions from the entire system, a method that samples the complex emission plume downwind of the operation, with measurements of the horizontal and vertical variability is necessary. The majority of studies conducted on animal feeding operations have looked at emissions no higher than 5 m (5m, Quinn et al., 2001; 2.6 m, Robarge et al., 2002; 2.4 m, Sommer et al., 2004; 5.2 m, Laubach and Kelliher, 2004), but emissions of most gases are still present at heights considerably above 5 m (Marcillac et al., 2006). ApSimon et al. (1994) modeled ammonia (NH_3) and nitric acid (HNO_3) gases in the atmosphere and showed that while both decreased with height, significant concentrations were still present up to 75 m. Erisman et al. (1988) found that measured ammonium (NH_4^+), HNO_3 and NH_3 concentrations decreased steadily with increasing height, and that NH_3 concentrations were still 25% of ground level (2m) concentrations at 200 m. These studies suggest that emission plumes from livestock operations can carry trace gases and aerosols to heights well above 5 m within a few meters of the emission sources. No system has been reported for use on livestock operations to measure concentrations at heights above 10 m; therefore, we conclude that a new sampling methodology is needed to fully measure vertical emission profiles from livestock operations.

We present a whole farm measurement system that overcomes these limitations by sampling concentration and meteorological profiles at various heights (up to 100 m) downwind of livestock operations to characterize the horizontal and vertical extent of the plume at relatively high temporal resolution (30-120 min). The system is designed to measure trace gases (carbon dioxide, methane, and nitrous oxide), and nitrogen species (nitric acid, ammonia, and ammonium). The objective of the study was to test the precision of the sampling equipment in the lab and field, demonstrate the efficiency of the system under field conditions, and present results of emission profiles obtained from measurements at a dairy.

MATERIALS AND METHODS

System Assembly

Set-up Overview

Our novel sampling system (Figure 4.1) employed four 15 to 21 foot tethered helium balloons (Blimp Works, Statesville, NC), three spaced downwind across the farm perimeter to characterize the emission plume and one upwind of the farm to characterize the local background concentrations and estimate trace gas enrichment by the farm. Gas, particulate, and meteorological sampling systems were attached to the blimp tether lines at five sample heights (2, 5, 10, 20, and 35 m). All blimps had the same five sample heights during a sampling period. Prior to attaching any equipment to the sample lines, balloons were deployed to a height of approximately 80 meters to avoid any effect on winds and turbulence conditions at the sample heights. The systems were mobile to allow flexible deployment based on wind directions.

Filter Packs

To collect NH_4^+ particulates, HNO_3, and NH_3, filter packs were used for sampling. Filter packs were attached to each tether line using aluminum rods (Vaisala, Boulder, CO). The filter pack inlet was left open to sample ambient air and the outlet was connected with Teflon tubing to a filter pump located on the ground. Five pumps, each regulated using a rotometer, were used on each tether to draw samples to the ground at a constant rate of 4 L m^{-1}. Rotameters were calibrated using a digital flow meter (DryCal DC-Lite 10 ml to 12 l, Bios International, Butler, NJ) before each use. Flow rates were carefully monitored such that the total volume of air sampled was known and could be used to determine particulate and gas concentrations following extraction of the filters. Due to lift weight limitations of the blimps (3.4 kg), commercial filter packs had to be modified to accommodate weight restrictions. Originally designed to hold just one filter, we modified the inside of each sampler (URG-2000-25F, Chapel Hill, NC) to hold three filters in a removable aluminum cartridge, each separated by a Teflon o-ring (URG-2000-25B) and a Teflon coated stainless steel screen (URG-2000-25ACT-1). The filter packs also contained an impaction plate at the inlet that had a particle size cutoff of 2.5 μm when operated at a flow rate of 4 L m^{-1}. Three different 25 mm filter types were used for sampling in order: Teflon (Zefluor, Pall Corp., East Hill, NY) for NH_4^+ particulates, nylon (Nylasorb, Pall Corp., East Hill, NY) for HNO_3, and phosphoric acid (H_3PO_4) coated cellulose (Whatman, Florham Park, NJ) for NH_3. All filter types were tested prior to use to verify they were devoid of any significant background concentrations of the species of interest. Additionally, blanks were run in the field to evaluate the quality of the data and estimate handling errors.

Filter handling and analysis. After sampling, filter packs were placed in an NH_3 free box and into a cooler to minimize evaporation from filters or background contamination. In order to extract the NH_4^+, HNO_3, and NH_3 from the Teflon, nylon, and cellulose filters, respectively, each filter was put into a 5 ml vial. Both the Teflon and cellulose filters were first wetted with 2 ml DDI and then sonicated in cold water for 50 minutes. The nylon filter was wetted with 2 ml of anion eluent (a sodium carbonate/sodium bicarbonate solution) and sonicated in cold water for 50 minutes. All of the extracts were analyzed by ion chromatography (IC, Dionex, DX-500).

Syringe Pumps

The less reactive gases, methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O), were sub-sampled from the main air stream using syringe pumps (New Era Pump Systems, Inc., Farmingdale, NY) at a rate of 1 ml min^{-1} and collected in 60 ml plastic syringes (Monoject, Kendall Healthcare, Mansfield, MA). Air not collected was released through an open t-tube at the end of the sample line.

Syringe handling and analysis. After collection, 30 ml of sample was injected into each of two evacuated exutainers (Labco Limited, UK). Exutainers were stored in a cool location out of direct sun exposure for 48 hours until analysis. The sample air was analyzed by gas chromatography (GC, Varian Corp.).

Meteorological Data

Detailed meteorological properties (wind speed, wind direction, temperature, relative humidity, and pressure) were measured at the five sample heights on the center downwind sampling station using a DigiCORA Tethersonde System (Vaisala, Boulder, CO). The tethersondes were attached to the tether line just above (30 cm) each filter pack. Data were relayed to a computer system at ground level in approximately 8 second intervals for the duration of each sample period. Wind direction data were analyzed to estimate the time that the wind direction and plume were in acceptable ranges for each downwind monitoring station (see Data Analysis).

Validation

Filter Packs

Laboratory testing. The modified URG filter packs were tested in the laboratory for system leakage as well as recovery of NH_3, HNO_3, and NH_4^+. The leak test was performed for NH_3 and HNO_3. For the test, HNO_3 was produced from a gas generator, and NH_3 from dissociation of ammonium nitrate (NH_4NO_3). Five filter packs were set up with three identical filters placed in line. For NH_3 collection, phosphoric acid coated cellulose filters were used, and nylon filters for HNO_3. A known amount of NH_4NO_3 (300 or 400 μg) or HNO_3 (500 or 600 μg) was released, and collected in unison by the filter packs for 5 to 10 h for NH_3, and 45 or 60 min for HNO_3. Each filter was analyzed for concentration to evaluate the collection efficiency of the filter pack. The total uncertainty in collection efficiency was expressed as (Karakas and Tuncel, 1997):

$$\% \text{ Collection Efficiency} = [(C_1 - C_2) / C_1] * 100 \qquad (1)$$

where $C1$ and $C2$ are the concentrations (μg) collected by the first and second filter, respectively.

Filter packs were also tested for collection of ambient HNO_3, NH_3, and NH_4^+ in the laboratory against a URG denuder system (URG-3000-C, Chapel Hill, NC) which is believed to give the best separation of particulates and gaseous species (Anderson and Hovmand, 1994). Sampling times were for 5 and 24 h. The filter pack was set up with three filters inline, Teflon (NH_4^+), nylon (HNO_3), and phosphoric coated cellulose (NH_3). The denuder was assembled with a cyclone at the air entrance with a particle size cut off of 2.5 μm, then two denuders inline, one coated with Na_2CO_3 for nitric acid recovery and the other with phosphoric acid for ammonia recovery. Lastly, a filter pack with a Teflon filter collected ammonium particulates prior to the sample air exiting the denuder system. Collection efficiencies were compared between the two systems.

Field testing. Filter packs were also field tested side-by-side for accuracy and efficiency of collection of NH_3, HNO_3, and NH_4^+ against the URG denuder system (Figure 4.1). For the field trial, one filter pack and one denuder system were set-up identically to the laboratory trials. A sampling trial was conducted on January, 30 2006 at a dairy operation in northeastern Colorado. Both filter packs and denuder samplers were located 2 m above ground level and 3 m from each other. Samples were collected for a one hour period from 1144 to 1244 h. Extracts from the filters and denuders were analyzed by ion chromatography, and compared for sampling efficiency.

System Field Trial

In order to display the unique properties of the system, a field sampling trial was conducted January 31, 2006 at a dairy located in northeastern Colorado. The dairy is a 1500 cow freestall operation with two small drylots, calving area, composting facility, and waste lagoon with preceding solid separation area (Figure 4.2). The freestall barns are flushed three times daily with recycled lagoon water that is channeled through open surface gutters to a leaky dam and settling basin solid separation system and finally into an anaerobic lagoon. The lagoon is an eight acre evaporation pond that had a significant crust buildup at time of sampling. An adjacent composting area receives all separated solids, drylot scrapings, straw used for bedding in drylot pens, and calf hutch waste. Sand bedding used in the freestall barns is collected from settling gutters leading from the barns to the solid separation and reused. Some small livestock operations were located near the dairy, but most land was in agricultural crops or developing suburban areas.

The sampling system was oriented the morning of sampling based on the mean wind direction. On the day of sampling, the wind was blowing from the SSE (average direction = 168°; Figure 4.2), contributing background air from Denver and other Front Range urban areas. Sampling was conducted for one hour from 1144 to 1244 h. Sampling periods are kept to one hour to maximize time in the dominant wind direction and to avoid filter saturation with NH_3 gas. Based on sonde wind data collected during the sampling period, we determined that the downwind sampling stations received air that had passed over the dairy surface 87% of the 60 minute sampling period.

After sample collection, filter packs were placed in NH_3 free boxes and stored for 12 h until analysis, and syringe samples were injected into two evacuated exutainers and stored until analysis. Ions collected on the filters were analyzed by IC, and greenhouse gases collected in syringes by GC.

Data Analysis

In order to account for dilution of samples with air not from the dairy plume (% of time the wind direction was not in the desired range), a set of calculations were developed to correct sample concentration for dilution.

First, using a map with tether locations plotted on it, we defined acceptable wind directions for each sampling location to include the minimum and maximum upwind directions that would bring air that had been within the farm perimeter. This was done by estimating the edges of the plume based on the location of the sampling station during a sampling period and the perimeters of the major contributing sources as they related to the sampling station. If the wind direction was in this range, it was considered a "good" measurement, contributing dairy emissions to the sampling station rather than background air. Next, a frequency distribution of wind directions for each sample height was created for the sampling period. For each height on each tether, we determined the fraction of time the wind was in the desired range for each sample. If the downwind sample location was in the desired range less than 40% of the time, no sample was accepted for this height and sample period. The minimum acceptable range was 60% for the upwind measurements. Once the fraction of time in the desired range was determined, the concentration values were adjusted for time. First, the upwind (background) concentration was adjusted using assumed regional ambient background concentration. This background concentration was determined by plotting measured seasonal values for each gas and taking the low value for the season. This value was then entered into equation (2) to determine an intermediate corrected downwind value,

$$DW^* = [(DW - BG^*) / f_{DW}] + BG^* \tag{2}$$

where DW^* is the intermediate corrected downwind concentration ($\mu g/m^3$), DW is the uncorrected downwind concentration ($\mu g/m^3$), BG^* is the determined background value ($\mu g/m^3$), and f_{DW} is the frequency of time the downwind location is in the desired range.

Once the downwind values were adjusted, the upwind values were similarly adjusted (3) using the primary corrected downwind concentration (DW^*),

$$UWa = [(UW - DW^*) / f_{UW}] + DW^* \tag{3}$$

where UWa is the adjusted upwind concentration (μg/m^3), UW is the uncorrected upwind value, and f_{UW} is the frequency of time the upwind location is in the desired range.

The adjusted upwind value (UWa) was finally used (4) to determine the adjusted downwind concentrations for each sample point,

$$DWa = [(DW\text{-}UWa) / f_{DW}] + UWa \tag{4}$$

where DWa is the adjusted downwind concentration (μg/m^3).

Lastly, the differential downwind concentration was determined by equation (5) to give the correct adjusted concentration increase related to farm emissions used in data analysis,

$$DW_{diff} = DWa\text{-}UWa \tag{5}$$

where DW_{diff} is the adjusted differential downwind concentration (μg/m^3). Corrections were done for each height at each sampling station.

Statistical Analysis

Data was tested for normality using the Shapiro-Wilk test for normality. Based on this test, data were found to be normality distributed and no transformation was needed. Data were then analyzed for differences between heights and sampling locations using PROC GLM in SAS (SAS, 1999). Differences were found using Tukey's procedure for pairwise comparison of means. Interactions were analyzed between height and location using contrasts. For NH_3 and HNO_3 efficiency analysis, total uncertainty was expressed as a percent of collection efficiency. Pearson's correlation coefficient (r^2) was used to measure the correlation between CO_2 and CH_4. Significance was evaluated at an alpha level of 0.05 for all analyses.

RESULTS AND DISCUSSION

Filter Pack Analysis

Laboratory Analysis

Laboratory leak tests showed that the filter packs had virtually no leakage (< 3%) around the modified filter apparatus for NH_3 and HNO_3. For NH_3, the filter packs had a 97.7% collection efficiency, and for HNO_3, a 98.5% efficiency. Karakas and Tuncel (1999) reported similar collection efficiencies of 95% for NH_3 and 98% for HNO_3 for a three stage filter pack. They found that as the concentration of NH_3 increased above 700 µg, their collection efficiency decreased to 85%. Since we did not test the filters above 400 µg, we can not confirm this finding.

When compared against a URG denuder system in the laboratory, the two systems had variable recoveries for each species. The recovery difference between the two systems was 16.7% for NH_3, 21.9% for HNO_3, and 4.4% for NH_4^+, with filter packs overestimating concentrations. Field comparisons of denuders and filter packs by Andersen and Hovmand (1994) found good collection efficiency of both NH_3 and NH_4^+. The authors reported a difference in collection between the two systems of 10 to 13% for NH_3 and 1 to 3% for NH_4^+, with filter packs overestimating concentrations. The overestimation of NH_3 and HNO_3 by the filter could be due to volatilization of NH_3 and HNO_3 from ammonium nitrate (NH_4NO_3) collected on the preceding Teflon filter (Park et al., 2004). Karakas and Tuncel (1997) found that nitric acid volatilized from ammonium nitrate particulates collected on the Teflon filters, erroneously increasing the concentration of nitric acid measurements by up to 20%. In general, they reported that, the quantity of NH_4^+ particulates collected on the Teflon filter, expressed in terms of gaseous pollutants, was about 10% of the NH_3 collected on the cellulose filter and 12 % of the HNO_3 collected on the nylon filter.

Field Analysis

Comparison of NH_3 and HNO_3 recovery between the filter pack and denuder systems in the field showed that the difference was greater than laboratory trials, 20% for NH_3 and 29% for HNO_3, with filter packs having a higher concentration than denuders for both compounds. This difference could be due to a number of reasons. In areas of high background NH_3, high temperatures, and low relative humidity, Andersen and Hovmand (1994) found that the filter pack method tended to overestimate NH_3 concentration by at least 10% over denuder concentrations. This could be due in part to evaporation of NH_3 from NH_4^+ particles collected on the preceding Teflon filter (Andersen and Hovmand, 1994; Karakas and Tuncel, 1997; Park et al., 2004). Karakas and Tuncel (1997) found that as NH_3 concentration under laboratory controlled conditions increased, the collection efficiency of acid coated cellulose filters decreased. The authors speculated that this was due to retention of NH_3 on the preceding nylon filter, which in field studies was sometimes up to 25% of the NH_3 collected on the cellulose filter based on temperature, relative humidity, wind speed, and wind direction. When compared against the denuder sampler, our filter packs had variable recovery rates for each species in the field, likely due to sampling artifacts from the filters, as well as handling error. On average we assume that our modified filter packs provide an acceptable recovery of NH_3 and HNO_3 concentration in the field.

System Field Trial

Meteorological Data

Meteorological data collected for each sampling height during the sample period are presented in Table 4.1. All parameters were relatively stable during the sample period. Wind direction data showed that the three downwind tethers were in the defined farm plume 86% of the time. Based on this, we could expect slightly lower recovery values than if the wind was in the plume 100% of the time, but the data is adjusted (equations 2 to 5) to reduce this bias.

Vertical Profiles

Differential concentrations (downwind minus upwind) for each measured species are shown by height in Figure 4.3. Results show that concentrations varied with height, and that each gas showed a distinct vertical profile, but only CO_2 ($P = 0.01$) and NH_3 ($P = 0.04$) were significantly different with height.

Similar to the profiles seen in the current study for NH_3 and HNO_3, ApSimon et al. (1994) and Erisman et al. (1988) both found that NH_3 concentration was greatest at ground level (2m) and decreased consistently and markedly with height. The consistent and significant decrease in NH_3 concentration with height in the current study demonstrates a significant source contribution from the dairy. Additionally, ApSimon et al. (1994) reported significant concentrations of NH_3 up to 75 m when measuring in open, natural areas. With concentrations of 41 μg m^{-3} still at 35 m, we could postulate that NH_3 concentration would continue to be above background levels at greater heights.

In Colorado, HNO_3 is one of the dominant background acidic species responsible for conversion of NH_3 gas to particulate NH_4^+ (i.e., ammonium nitrate). We expected HNO_3 concentration to have negative differential downwind values indicating either dry deposition to the ground surface or more likely, consumption with NH_3 and conversion to ammonium nitrate. Instead, HNO_3 was found to increase after passing over the dairy. Since we don't consider the dairy a source of HNO_3, we can assume that either the nitrate had volatilized from the particulate ammonium nitrate collected on the preceding Teflon filter (Park et al., 2004), or that the sample time was not long enough to collect a sufficient sample of HNO_3 to determine if concentrations were significantly different from background air. The vertical profile of HNO_3 (Figure 4.3) showed a trend of a sharp decrease in HNO_3 concentration at ground level (2 m), and then a fairly consistent profile above 5 m. This could indicate either deposition to the ground surface or consumption at ground level where NH_3 concentration was the highest. ApSimon et al. (1994) modeled the emission profile of HNO_3 and also found that concentrations decreased sharply at ground level due to high surface deposition velocity, but after about 25 m, were stable, varying by only 1 to 2 μg m^{-3} up to 200 m. Erisman et al. (1988) showed similar results measuring lower HNO_3 concentrations up to 25 m, and increasing concentrations above that. We suggest that since NH_3 concentration is so high near the ground surface, virtually all the background HNO_3 reacts with NH_3 to form NH_4^+ particulates. The increasing trend of HNO_3 concentration above 5 m is likely due to a reduction in interaction with NH_3.

Ammonium concentration has been shown to vary little with height (Erisman et al., 1988; ApSimon et al., 1994), with concentration varying by only 25% between 2 and 200 m (Erisman et al., 1988). In the current study, the formation of NH_4^+ particulates is reflected in the high percentage of total NH_4^+ concentration (50%) that is found at or below 5 m, and the steady profile above 5 m (Figure 4.3). The increased concentrations of NH_3 (59%) and HNO_3 (43%) at and below 5 m, are likely contributors to the high rate of NH_4^+ particulate formation at this same level.

Since the dairy does not provide a significant sink for greenhouse gases, just a source, and since sampling stations were located adjacent to the major emitting sources of greenhouse gases (i.e. lagoon, compost, and barns), we would have expected to see an increase in concentration at or near ground level, with steady or decreasing concentrations above that. However, trends in the profiles of the greenhouse gases (CO_2, CH_4, N_2O) emitted from the dairy all showed similar profiles with an increase in concentration up to 20 m, which was the peak concentration, then a decrease above 20 m, with more than 40% of emissions collected at or above 20 m. Peak concentrations at 20 m could indicate that the greenhouse gases were collected at greater heights possibly due to lack of interaction at lower levels, which could deplete the gases at a faster rate. Additionally, collection at greater heights could have possibly been due to turbulence associated with farm buildings, which could lead to divergent profiles. Either way, less reactive greenhouse gases should be collected at greater heights to ensure adequate sampling.

Additionally, a strong correlation ($r^2 = 0.71$; $P = 0.04$) was observed between CO_2 and CH_4 profiles. A similar correlation ($r^2 = 0.70$) was found by Kinsman et al. (1995) for emission between these two gases from dairy barns. The strong correlation is due to similar primary sources of respiration (CO_2) and eructation (CH_4) from cows, both of which are affected by diet and management rather than external conditions (i.e., weather) (Kinsman et al., 1995; Johnson and Johnson, 1995; Jungbluth et al., 2001). The correlation is also seen in the vertical profiles of these two gases (Figure 4.3) and major source contributions (Table 4.2).

Downwind Station Variation

The three monitoring stations placed downwind of the sample dairy were all picking up difference source plumes (Figure 4.2) due to the close proximity of the sample locations to the dairy perimeter. (Normally, a distance of 200 m is suggested from sampling sources to ensure adequate mixing of plume sources; however in this case, that was not possible due to land use restrictions). The average concentration of all three stations is considered the mean downwind concentration (Table 4.2); however, some significant differences were found between sampling station locations (Table 4.2) so individual analysis of each sampling station is necessary.

For CO_2, CH_4, and N_2O, significant differences were found between sample locations. In all cases, downwind location 1 (DW1) had significantly ($P = 0.01$ CO_2, $P = 0.03$ CH_4, $P = 0.04$ N_2O) higher concentrations compared to downwind location 2 (DW2) and 3 (DW3), which were not different from each other ($P > 0.05$). The primary source contributor to DW1 was the freestall barns (Figure 4.2), a significant source of CH_4 and CO_2 (Kinsman et al., 1995). While N_2O was highest at DW1, its second highest concentration was at DW2, which was located downwind of the composting area, a significant source of N_2O (Hao et al., 2001, 2004; Paillat et al., 2005). The second highest contributing source for CO_2 and CH_4 was DW3, the lagoon. The lagoon is considered a significant source contributor of CH_4 emissions (Phetteplace et al., 2001; Amon et al., 2006), but not CO_2. The differences in sample locations are taken into account when all stations are pooled together to compile one sample concentration; however, it is important to be aware of differences in concentrations with location and plume source.

Similar to the three greenhouse gases, NH_3 tended ($P = 0.12$) to be higher at DW1 (Table 4.2), whose major source contribution was the freestall barns. Housing is considered one of the greatest sources of NH_3, with 24 to 50% of excreted nitrogen volatilizing as NH_3 in the barn (Pollet et al., 1998; Amon et al., 2001; Moreira and Satter, 2006). The other sample locations had similarly low levels of NH_3 concentration.

Both HNO_3 ($P = 0.89$) and NH_4^+ ($P = 0.95$) had very little variation between sample locations. Since HNO_3 is mainly contributed by background air and is, thus, evenly distributed among sample locations, and NH_4^+ is largely produced from NH_3 on farm or already present in background air, this trend is to be expected.

The use of multiple downwind locations allows the quantification of area sources, while still characterizing the entire operation. However, replication of source data requires the same consistent wind direction and speed, which can be difficult to obtain over seasons, and even throughout a day. It is simpler to infer whole plume characteristics throughout the year, rather than sources, when using this method.

System Analysis

While the system worked well under field conditions, changing wind directions and unfavorable weather patterns could compromise sampling times. The system can not operate safely or efficiently in winds above 9 m s^{-1}, rainy weather, or under overcast skys that might introduce downdrafts. Additionally, changing wind directions, or lack of wind, doesn't allow a good sample collection of air from the dairy, and so sampling must be stopped and stations moved or restarted under more favorable conditions. Ideal operating conditions are clear days with a consistent wind direction and wind speed. Under these ideal conditions, the system is easy to use and provides a novel collection of whole plume concentrations from livestock operations.

CONCLUSION

The air sampling methodology outlined here has been demonstrated as an effective means of collecting NH_3, HNO_3, and NH_4^+ with modified filter packs, as well as CO_2, CH_4, and N_2O with syringe pumps. The use of weather monitoring equipment (i.e. tethersondes), is vital to the validity of this data, as the wind speed dictates the spread of the plume, the wind direction the collection efficiency, and the temperature, pressure, and RH the concentration of the gas or particle species. We have illustrated that the vertical profiles of several species collected varied with height, and that profiles are fairly consistent with atmospheric predictions. The concentrations found above 10 m indicate a need to sample at greater heights when looking at whole-farm plumes than has traditionally been done. The data provided by this system could prove to be a very valuable tool in selecting monitoring heights for different gas and particle species.

Table 4.1. Mean meteorological data by height for the sampling period

Height (m)	Pressure (mbar)	Temperature (°C)	Relative Humidity (%)	Wind Speed ($m\ s^{-1}$)	Wind Direction (°)	% Time in Desired Range	
						Upwind	Downwind
35	832	3.40	22.61	2.57	165.6	88.0	85.3
20	834	3.51	21.50	2.31	163.3	87.5	85.0
10	835	3.71	21.13	2.14	162.9	89.9	89.3
5	836	4.07	20.65	1.93	163.1	82.0	80.6
2	836	4.33	20.24	1.85	168.2	91.3	89.3
Mean	*835*	*3.80*	*22.03*	*2.16*	*164.6*	*87.7*	*85.9*

Table 4.2. Mean concentrations and standard deviations (in parentheses) for each species by downwind sampling location and total average concentration

Sample Station[a]	CO_2 (μg m^{-3})	CH_4 (μg m^{-3})	N_2O (μg m^{-3})	HNO_3 (μg m^{-3})	NH_3 (μg m^{-3})	NH_4 (μg m^{-3})
DW1[b]	50906.2(12319.6)a	286.2(44.5)a	39.01(15.22)a	0.67(0.18)	123.44(45.21)a	0.25(0.22)
DW2	39350.0(14892.0)b	105.1(46.9)b	17.97(8.46)b	0.54(0.21)	94.86(62.38)ab	0.30(0.21)
DW3	46876.6(15325.0)b	115.1(47.9)b	14.44(8.65)b	0.83(0.37)	57.20(22.05)b	0.25(0.23)
$Pr > \|t\|$[c]	*0.01*	*0.03*	*0.04*	*0.89*	*0.03*	*0.95*
UW, avg[d]	597,811.0(13,440.1)	1062.7(49.7)	536.09(9.97)	0.19(0.004)	12.33(0.48)	0.45(0.09)
DW, avg[e]	45,710.9(14,161.3)	168.8 (98.2)	23.81(15.30)	0.68(0.28)	91.8(51.2)	0.26(0.20)

[a] Sampling stations were downwind 1 (DW1), 2 (DW2), and 3 (DW3).

[b] Different letters, a, b, denote significant differences ($P < 0.05$) within each column.

[c] P-values were assessed between sample stations for each species at a significance level of $P < 0.05$.

[d] Mean upwind (UW) concentrations averaged across all sampling locations.

[e] Mean downwind (DW) differential concentrations averaged across all sampling locations.

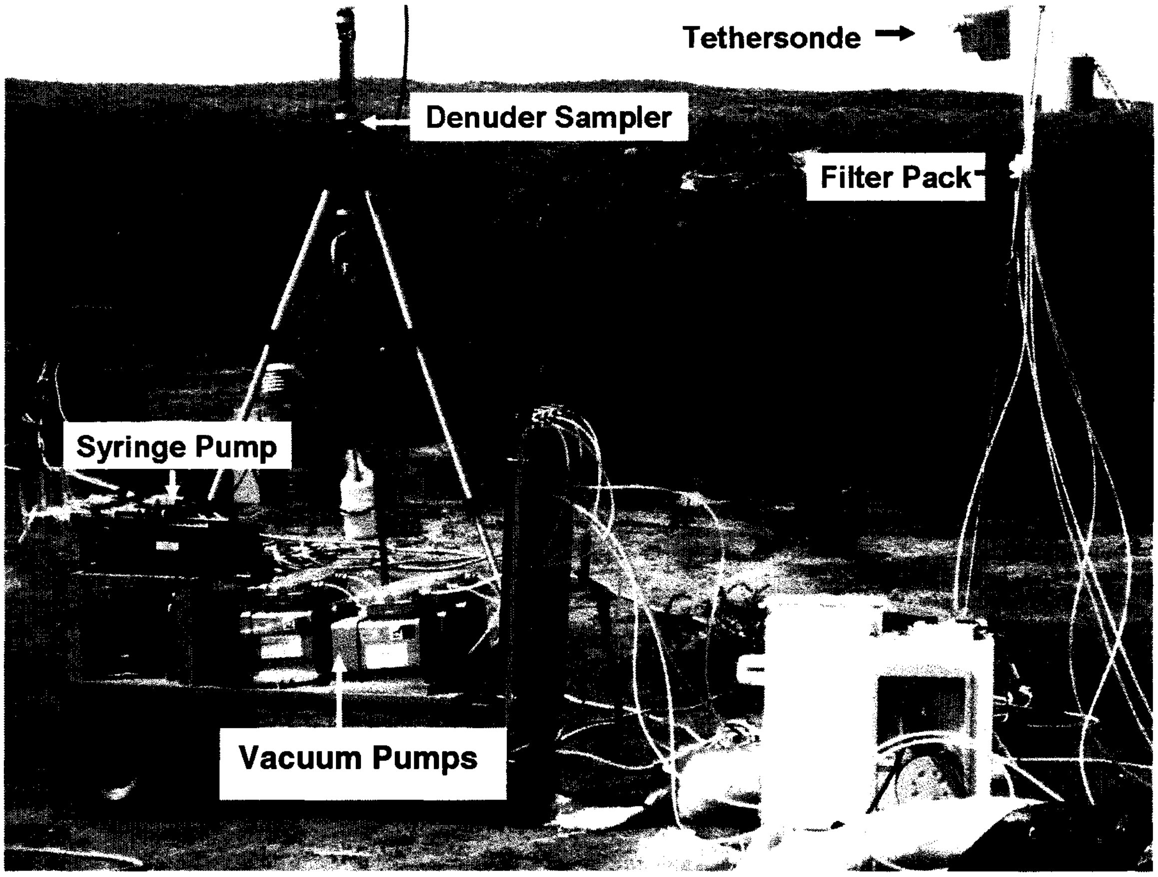

Figure 4.1. Emission sampling system for plume characterization. The sampling system uses helium balloons to loft filter packs (NH_3, HNO_3, NH_4^+), sample lines and meteorological samplers (tethersondes) to multiple (5) heights in the lower atmosphere downstream of the target CAFO. Teflon tubing is run to the ground to vacuum pumps sampling at a known flow rate (4 l min^{-1}) such that total air sampled by the filter packs is known. A syringe pump is then used to sub-sample from the main air flow to collect air samples for analysis of greenhouse gases (CO_2, N_2O, CH_4). Four of these systems are deployed on each occasion to sample the upwind (1) and downwind (3) plume structure. A denuder sampler was set up adjacent to the system to validate filter pack recovery.

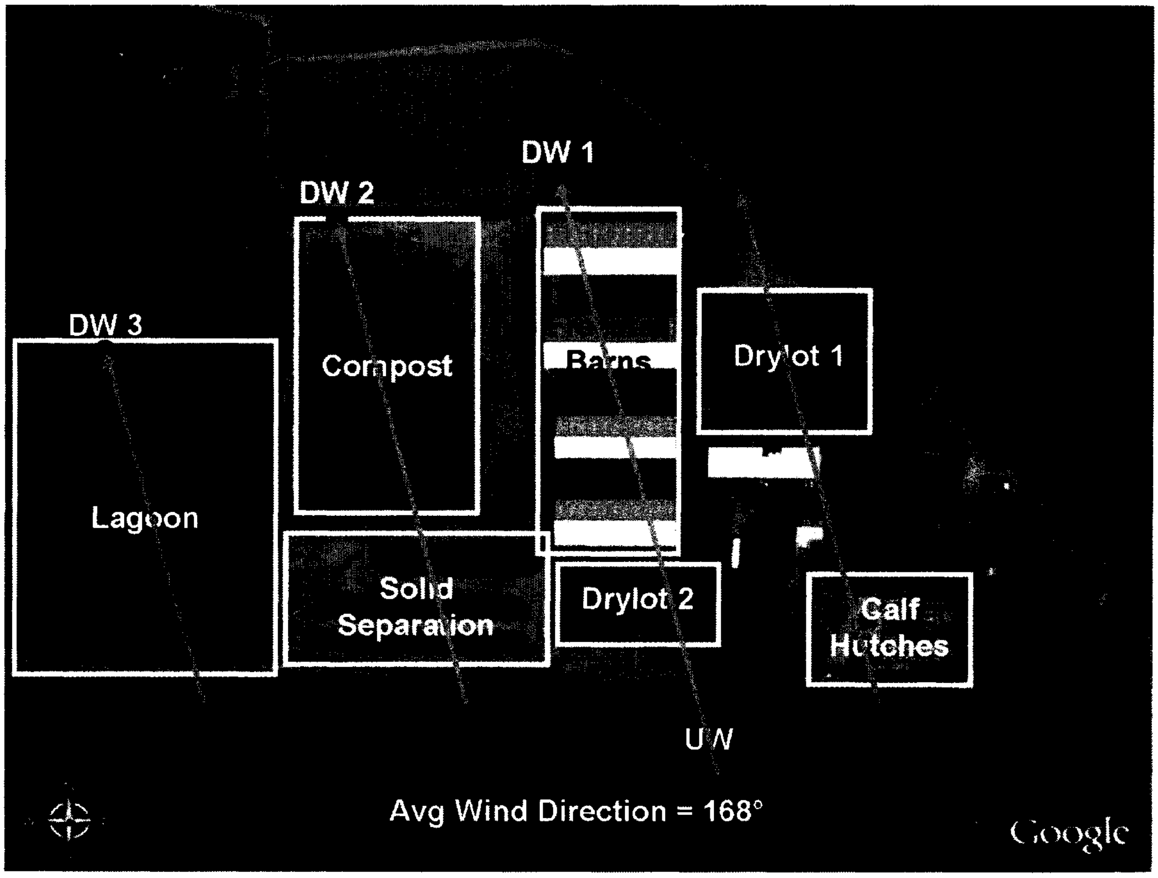

Figure 4.2. Map of the sample dairy layout. Boxes outline major emission areas of the dairy. Dots represent the sample locations (DW = downwind, UW = upwind). Bold lines represent the average wind direction (168°) as it relates to the sample location. (Image obtained from Google Earth).

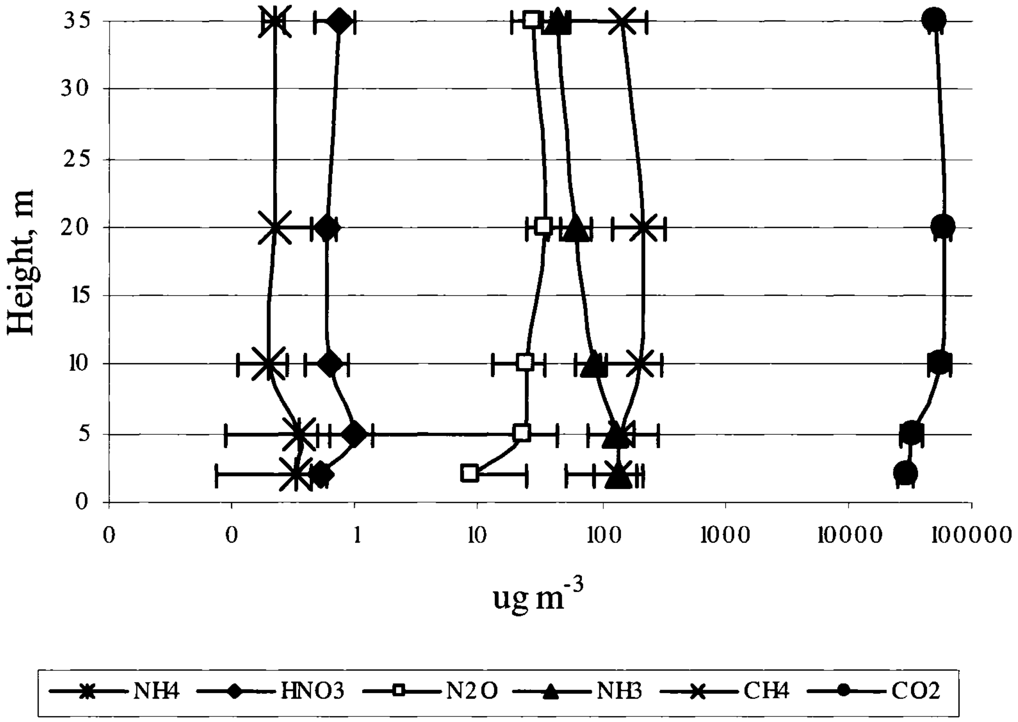

Figure 4.3. Downwind average vertical enhancement profile of ammonium (NH_4), nitric acid (HNO_3), nitrous oxide (N_2O), ammonia (NH_3), methane (CH_4), and carbon dioxide (CO_2). Concentration differences (downwind-upwind, ug/m^3, averaged across three tethers) are presented on a log scale to present each species on the same graph.

CHAPTER V

CHARACTERIZATION AND QUANTIFICATION OF AIR EMISSIONS FROM DAIRIES

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ABSTRACT

Animal agriculture is a major source of atmospheric pollutants, but the nature and dispersion of those pollutants are not well understood. Additionally, little data is available on the vertical profile of emissions since few studies have looked at emissions above 10 m. The aim of this study was to quantify emissions of ammonia, ammonium, nitric acid, methane, carbon dioxide, and nitrous oxide from dairy systems, and characterize the spatial, diurnal, and seasonal variability of those emissions. Using a unique mobile sampling methodology employing helium balloons, filter packs, syringe pumps and a tethersonde meteorological sampling system, gases and particulates were measured at five heights (2, 5, 10, 20, 35 m) at three locations downwind and one location upwind of two dairies. This innovative technique provided a spatially (vertically and horizontally) resolved characterization of the emission plume. Measurements were made seasonally at two dairies from summer 2005 to winter 2006. Results show that the concentration of each species varied vertically and seasonally, and that each dairy had its own distinct profiles. Seasonally, the greenhouse gases tended to follow similar patterns with maximum concentrations in the winter months, while ammonia was highest in the summer. Despite differences between the two diaries, maximum concentrations were commonly found at or near ground level (2 m) indicating a strong emission source from the dairy. Above 2 m, ammonia exhibited the most consistent vertical profile, which steadily decreased with height ($P = 0.04$) up to 35 m; however background levels were not reached indicating that concentrations were still likely to be significant above 35 m. This study characterized the seasonal, diurnal, and spatial variability of emissions from two dairy operations, which are important considerations when measuring and modeling gaseous emissions for scientific or regulatory purposes.

Keywords: Dairy, Emissions, Ammonia, Greenhouse gases, Whole farm plume

INTRODUCTION

Animal agriculture, especially dairying, is being targeted as a significant source contributor of atmospheric pollutants. The major pollutants of concern are ammonia (NH_3), ammonium (NH_4^+) particulates, methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2). Each of these compounds has specific concerns to public health and/or environmental impacts, which is why they are of interest to researchers and regulators alike.

Globally, agriculture is the largest contributor of atmospheric NH_3, with animal agriculture accounting for approximately 40% of total NH_3 emissions, and crop agriculture contributing an additional 23% from synthetic fertilizer application and soil emissions (Bowman et al., 1997; EPA, 2005). The adverse effects of atmospheric ammonia include environmental consequences such as particulate formation resulting in decreased visibility, natural ecosystem changes, water eutrophication, and soil acidification (de Boer, 2003; Krupa, 2003; Baron, 2006). The primary source of ammonia production on livestock operations is the combination of urea in urine with the urease enzyme in feces or soil which rapidly hydrolyzes to form NH_3 gas. The reaction is relatively rapid, taking anywhere from 2 to 10 hours for NH_3 volatilization to peak after mixing of urine and feces (Muck, 1981; James et al., 1999). The actual quantity and rate of NH_3 volatilization from manure depends on a variety of factors including dietary crude protein level, manure management techniques, pH, ambient temperature, relative humidity, and wind speed (Muck, 1982; Voorburg and Kroodsma, 1992; Robarge et al., 2002; Beck et al., 2004; Cole et al., 2005; Zhang et al., 2005). While we know that ammonia emissions are most affected by temperature (Robarge et al., 2002; Cole et al., 2005), the atmospheric behavior of ammonia above 10 m is not as well known.

Ammonia has a relatively short lifetime (< 24 h) with major loss pathways through dry deposition close to the source and chemical reaction with acidic gases in the atmosphere, including nitric and sulfuric acid, to form particulate ammonium salts (ammonium nitrate and ammonium sulfate, respectively) (Baek et al., 2004). Ammonium particulates are a type of fine particulate matter or $PM_{2.5}$ (particles less than 2.5 microns in diameter). Due to their small diameter and increased atmospheric lifetime (~15 days), these fine particulates are able to travel longer distances before dry or wet deposition to the ground surface occurs. Given the right meteorological and atmospheric conditions, these small particles can travel from agricultural areas to pristine mountain ecosystems (Fenn et al., 2003; Baron, 2006) or urban locations where they can mix with other pollutants and accumulate in the atmosphere, contributing to decreased atmospheric visibility (Finlayson-Pitts and Pitts, 2000) and respiratory human health issues (Merchant et al., 2003).

Unlike ammonia and ammonium particulates, greenhouse gases such as CH_4, N_2O and CO_2 are regarded as global concerns due to their long atmospheric lifetimes (10, 150, and 100 years, respectively), low volatility, and contribution to global climate change (Godish, 2004). Globally, the EPA (2005) estimates that ruminant livestock contribute 30% of the total CH_4 budget. The majority of that CH_4 (75%) is produced during ruminant enteric fermentation. Enteric fermentation is the microbial digestion of cellulose in the rumen, which is released as CH_4 gas by eructation. The rate of enteric fermentation is largely dependent on animal diet (Johnson and Johnson, 1995) rather than climatic conditions. The other 25% of CH_4 emissions from livestock is produced from anaerobic decomposition of organic matter in manure and anaerobic waste lagoons, which contributes 9.8% of the total US CH_4 budget and has been shown to vary with season and management technique (Wuebbles and Hayhoe, 2002). However, like ammonia, the vertical profile of methane is not well characterized above 10 m.

The exact contribution of N_2O and CO_2 emissions from dairies is uncertain. The processes of agricultural tillage, fertilizer use, and animal waste treatment account for about 39% of total global N_2O emissions (Oenema et al., 2001), and 68% of US N_2O emissions (EPA, 2005). However, of the total emissions from agricultural sources, livestock manure management and anaerobic denitrification processes only contribute to about 6% of the total N_2O emissions (EPA, 2005). Like N_2O, agriculture contributes a very small amount (0.4% yr^{-1}; IPCC, 2001) to the CO_2 budget, and livestock are not even considered by the EPA (2005) as a significant source of CO_2. The main sources of CO_2 from livestock operations, besides emissions from vehicles, would be direct CO_2 exhalation from cows (Jungbluth et al., 2001) and composting (Hao et al., 2004; Paillat et al., 2005). Overall, the on-farm sources of CO_2 are not well characterized, nor are the emission profiles.

Up until now, emissions from dairy operations have been characterized using methods such as flux chambers (Eklund, 1992; Aneja et al., 2000; Sommer et al., 2006), remote sensing (Rumburg et al., 2004; Shores et al., 2005; Laubach and Kelliher, 2005), and modeling (Kohn et al., 1997; Pinder et al., 2004), but each has shortcomings when trying to characterize an emission plume from a whole operation. The limiting factor of these methods is that they generally do not provide measurements for an entire livestock operation nor for multiple gases, but rather measure components of the whole system. Additionally, the majority of studies conducted on animal feeding operations have measured concentrations no higher than 5 m (5m, Quinn et al., 2001; 2.6 m, Robarge et al., 2002; 2.4 m, Sommer et al., 2004; 5.2 m, Laubach and Kelliher, 2004), but turbulent transport in the atmospheric boundary layer results in most gases still being present at heights considerably above 5 m (Erisman et al., 1988; ApSimon et al., 1994; Marcillac et al., 2006). In order to characterize emissions from the entire system, a method that samples the complex emission plume downwind of the operation, with measurements of the horizontal and vertical variability of the plume is necessary (Chapter 4, this dissertation).

The current study was designed to quantify concentrations of NH_3, NH_4^+, HNO_3, CH_4, CO_2, and N_2O from dairy systems using a novel vertical sampling technique employing mobile helium balloons (Chapter 4, this dissertation). Additionally, we examined the vertical and horizontal characteristics of the plume, as well as the diurnal and seasonal variability of each species.

MATERIALS AND METHODS

General

Sampling was carried out seasonally, from summer 2005 to fall 2006. Measurements were taken for one hour, three times per day (at approximately 0700, 1100, and 1500 h), for two days at each location, over four seasons at each of two dairies in Colorado. The two dairies monitored had contrasting housing strategies, freestall (Dairy 1) (Figure 5.1) and drylot (Dairy 2) (Figure 5.2), but similar manure management systems (flush lanes, leaky dam and settling basins, open lagoon storage, and composting). Additionally, the lagoon at Dairy 1 was also partially aerated. While a sufficient crust was present over the lagoon over for most of the year, 16 small bubblers in the lagoon introduced oxygen and algae (AgSmart Inc., Strasburg, CO) into the lagoon year round, effectively aerating a small portion of the lagoon. Dairy 1 had 1500 cows and Dairy 2 had 2000 cows.

Sampling System Design

Gases were measured using a unique sampling system (Chapter 4, this dissertation) specially designed for this project and included ammonia (NH_3), ammonium (NH_4^+), nitric acid (HNO_3), methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (N_2O). The system employed four 6.4 m long tethered helium blimps (Blimp Works, Statesville, NC); three spaced downwind across the farm perimeter and one upwind. Gas, particulate, and meteorological sampling systems were attached to the blimp tether lines at five sample heights (2, 5, 10, 20, and 35 m) for downwind and three sample heights (2, 10, and 35 m) for upwind locations. Highly reactive gases (NH_3 and HNO_3) and particulates (NH_4^+) were collected using filter packs attached at each height, with less reactive gases (CH_4, CO_2, and N_2O) pumped to the ground and collected using syringe pumps. Detailed meteorological properties (wind speed, wind direction, temperature, relative humidity, and pressure) were measured in eight second intervals at the five sample heights on the center downwind sampling station using a DigiCORA Tethersonde System (Vaisala, Boulder, CO). The tethersondes were attached to the tether line just above (30 cm) each filter pack. The blimps and all sampling equipment were assembled on trailers so the system could be mobile to accommodate changing wind directions. This sampling technique was designed to overcome the limitations of other height-restricted, stationary sampling systems and provide a spatially (vertically and horizontally) resolved characterization of the emission plume. (Further information about the system set-up and analysis can be found in Chapter Four (this dissertation).

Data Analysis

Since data reported are in differential total concentrations (downwind minus upwind), some adjustment needed to be made to account for the changing wind directions during sampling. First, we defined acceptable wind direction ranges for each sampling location for each sampling period. This was done by estimating the edges of the plume based on the location of the sampling station during a sampling period and the perimeters of the major contributing sources as they related to the sampling station. If the wind direction was in this range, it was considered a "good" measurement bringing emission from the dairy to the sampling equipment rather than background air. Next, a frequency distribution of wind directions for each sample height was created for each sampling period. For each height, we determined the fraction of time the wind was in the desired range for each sample. If the downwind sample locations were in the desired range less than 40% of the time, no sample was accepted for this height and sample period. The minimum acceptable range was 60% for the upwind measurements. A more stringent range was set for upwind to avoid contamination of background air with emissions from the dairy. Of all the samples taken, 100% of the upwind samples were in the desired range, and 87% of the downwind samples were acceptable.

Differential concentrations were found for each sample point using the set of equations found in (Marcillac et al., 200X). [Chapter 4 (this dissertation)].

Statistical Analysis

Due to the large variation in management techniques between Dairy 1 and Dairy 2, each dairy was analyzed independently, but variation was analyzed between dairies to illustrate variability among operations. Normality was assessed using the Shapiro-Wilk test for normality. Based on the results, no transformation of data was necessary. Preliminary statistical analysis was conducted on the data to identify significant interactions between season, height, location, and sample time using a MIXED model in SAS (SAS, 1999). Data were then analyzed for differences between seasons, heights, sample time, downwind sample locations, and meteorological parameters using a MIXED model. Due to missing values, significant differences within each parameter were assessed using Tukey's comparison of means adjusted by the least squares means (LSMEANS), which is an analysis of means for unbalanced designs. Correlations were assessed using correlation coefficients (r^2) to assess the relationship between height and NH_3. All significance was evaluated at an alpha level of 0.05.

RESULTS AND DISCUSSION

Meteorological Data

Meteorological differences are important when assessing the seasonal emissions of different gas and particle species. The use of weather monitoring equipment (tethersondes used here) was vital to the analysis of the data; the wind speed dictated the spread and dilution of the plume, the wind direction the collection efficiency and source of emissions, and the temperature, pressure and RH the concentration of the gas or particle species.

Seasonal characteristics. Meteorological data are presented by season for each dairy in Table 5.1 to illustrate the differences in seasonal conditions. There were no significant differences ($P > 0.40$) between dairies or season within dairy ($P > 0.05$) for any of the meteorological variables except for temperature, which was significantly different ($P < 0.001$) between seasons at each dairy.

For Dairy 1 the greatest temperatures were measured in the summer and spring, which were similar to each other, but higher than winter temperatures, which were the lowest. Dairy 2 also had the highest temperatures in the summer which were higher than winter temperatures, which were also the lowest. Seasonal temperatures at both dairies were not significantly different ($P > 0.05$) from average historical seasonal temperatures for Colorado (data not shown). However, when compared between dairies, average summer temperatures at the two dairies were significantly different ($P = 0.001$) from each other. Spring average temperature was also significantly different ($P = 0.001$) between the two dairies. Winter temperatures were not different ($P = 0.23$).

The dominant wind direction varied diurnally for all seasons, but seasonal averages show that there was no difference between average seasonal wind directions for either dairy ($P = 0.85$). However, diurnal shifts in wind direction varied among and within seasons, affecting the location of the sampling stations. This was important to note because wind direction dictated where background air came from and what the primary source contributors were for each station during each sampling period. These differences affected the variation in concentrations collected among sampling stations during each sampling period. Using the mean value of the concentration for all sampling stations over the sampling period should account for variations in location concentration, but shifting locations did introduce some variability into the data.

Vertical profiles. The vertical profiles of pressure, temperature, relative humidity, and wind speed all were significantly different ($P < 0.001$) with height (data not shown). At both dairies, pressure and temperature decreased with increasing height. Relative humidity had a curvilinear profile at both locations with highest values at the top and bottom heights. Wind speed only demonstrated significant differences with height ($P = 0.001$) at Dairy 1, but both diaries showed a trend of increased wind speed with increasing height. Wind direction was variable with height and showed no distinct vertical pattern at either dairy.

Diurnal variation. At Dairy 1, a significant difference existed among sample times (morning, noon, and afternoon) for pressure ($P = 0.001$), relative humidity ($P = 0.006$), and wind speed ($P = 0.05$). Pressure was significantly different for each sample time and decreased over the course of the day. Relative humidity was highest in the morning, and steadily decreased throughout the day, each sampling time being significantly different from the previous sampling time. Wind speed demonstrated an increasing trend over the course of the day with afternoon wind speeds significantly higher than other sampling times.

Dairy 2 also had a similar significant diurnal variation in relative humidity ($P = 0.004$), as well as temperature ($P = 0.004$), but not pressure ($P = 0.23$) or wind speed ($P = 0.31$).

While they were only significant at Dairy 2, both dairies showed lower ambient temperatures in the morning sampling hours than in the hotter late afternoon.

Concentration Data

Upwind

Upwind data are presented by season for each dairy in Table 5.2. Upwind greenhouse gas concentrations for each dairy were higher than estimated background values (Table 5.2), indicating that regional background concentrations were higher than global predictions for greenhouse gases. Local background concentrations of HNO_3, NH_3 and NH_4^+ were not available, so we consider our upwind values as the local background concentrations.

Seasonal characteristics. Seasonal patterns in upwind values were different between dairies and species (Table 5.2), but not significantly. Except for NH_4^+ at Dairy 1 ($P = 0.004$) and HNO_3 at Dairy 2 ($P = 0.007$), there were no significant differences in upwind concentrations by season within either dairy ($P > 0.05$).

Background NH_4^+ concentrations were highest in the winter at Dairy 1 and lowest in spring and fall. Since both seasons had similar dominant wind directions, this is likely due to the equilibrium shift in the partitioning between ammonium particulates (i.e. NH_4NO_3) and their gas phase components (i.e. NH_3 and HNO_3 gases), since the more stable particulates are favored during cooler temperatures (Walker et al., 2006). Therefore, more ammonium particulates would be expected to be present in background air at highest concentration in the colder winter months, and inversely the lowest concentrations should be observed in the hotter summer months.

The high HNO_3 background concentrations during spring at Dairy 2 were likely due to the close proximity to Denver, CO and the seasonal prevailing winds. During the spring, the prevailing wind direction was from the WSW, which brings background pollutants from the Denver metro area directly to Dairy 2. Dairy 1 saw a similar relationship with more southern wind directions bringing urban pollutants toward the dairy from the northern Front Range area during the summer and fall, but the results were not significantly different. Additionally, we would expect to see higher HNO_3 concentrations in background air in the summer due to enhanced photochemistry in the atmosphere.

The upwind seasonal patterns for each measured gaseous species were different for each dairy, indicating that background emissions and upwind source contributors varied with geographical location within season. For instance, upwind HNO_3 and NH_3 concentration tended to be higher at Dairy 2 during the spring and winter, likely due to the close proximity of Denver, CO and a greater number of livestock operations within 20 miles of the dairy. However, when averaged over the course of the year, mean annual upwind concentrations between the two dairies were not significantly different ($P > 0.05$). Additionally, we found that seasonal upwind concentrations did not mimic seasonal downwind patterns at either dairy (Table 5.2 and 5.3). This would indicate that on-farm emissions from dairies do not follow seasonal background trends and are subject to variations in management techniques on the operation. This demonstrates the importance of characterization of background sources when looking at whole farm plume emission and on-farm reactions (i.e. ammonium nitrate formation).

Vertical profile. For the most part, the vertical profiles for upwind concentrations were not significantly different with height (data not shown). However, Dairy 1 had a significant ($P = 0.04$) decrease in CH_4 concentration with increasing height, and Dairy 2 had a significant ($P = 0.003$) decrease in NH_3 concentration with increasing height. Other gases showed consistent profiles (< 10% variation) with height, with no significant differences within the vertical profile.

Diurnal variability. No significant diurnal variation ($P > 0.05$) was found in upwind concentrations at either dairy (data not shown). However, trends showed that background NH_3, CH_4, and CO_2 concentrations tended to increase over the course of the day at both dairies. Nitrous oxide, HNO_3, and NH_4^+ showed no diurnal patterns at either dairy.

Downwind (On-farm Concentrations)

Seasonal characteristics. Due to weather constraints (rain and early snowfall), no fall data are available for Dairy 2. Seasonal trends in downwind differential concentrations differed between the two dairies (Table 5.3). For Dairy 1, we found that concentrations varied differently for each species within season, but only CO_2 had significantly different ($P = 0.04$) concentrations by season. While other studies have found that CH_4 exhibits a seasonal trend of higher emissions in warmer months and lower in cooler months (Wuebbles and Hayhoe, 2002), we found that CH_4 along with CO_2 had the highest concentrations in the winter followed by spring months, but for both dairies a predictable seasonal trend was not clear. Jungbuth et al. (2001) reported that neither CH_4 nor CO_2 showed any seasonal emission pattern, but similar to our results, the two were emitted in similar patterns. A similar relationship was also observed by Kinsman et al. (1995) who found a strong correlation ($r^2 = 0.70$) between CH_4 and CO_2 emissions from dairy cattle. The lack of seasonal pattern in this study was likely because the majority of CH_4 (75%;

EPA, 2005) was emitted directly from ruminant animals via enteric fermentation, and is greatly affected by animal diet, animal numbers, and management (Johnson and Johnson, 1995), rather than by season. Additionally, the large seasonal variation in CO_2 emissions was likely due to the variation in sources rather than seasons. The primary source of CO_2 was direct emission from animal digestion and respiration, which is not affected by season (Kinsman et al., 1995; Jungbluth et al., 2001). Smaller contributing sources, which have some seasonal variability, are aerobic composting processes and fossil fuel combustion. Additionally, some CO_2 was produced along with NH_3 from urea hydrolysis, which occurs when urine urea ($(NH_2)_2CO$) combines with urease in feces and soil and rapidly hydrolyzes as NH_3 gas and carbamine acid (NH_2COOH), which decomposes to release NH_3 gas and CO_2 (1).

$$(NH_2)_2CO + H_2O + \text{urease} \rightarrow NH_2COOH + NH_{3\,(g)}$$

$$NH_2COOH \rightarrow NH_{3\,(g)} + CO_{2\,(g)} \qquad (1)$$

The reaction only produces about half the amount of CO_2 to NH_3, but this amount could be a significant contributing CO_2 source considering that of the total nitrogen excreted in manure (70% of the N intake, Wilkerson et al., 1997; Webb, 2001), 41 to 54% is excreted as urinary urea nitrogen in lactating dairy cows (Wilkerson et al., 1997; James et al., 1999; Van Horn et al., 2004), and 72% is volatilized as NH_3 (James et al., 1999). This would mean that up to an estimated 36% of urinary urea could be volatilized as CO_2 during the urea hydrolysis pathway described in (1). Overall, compared to upwind concentrations which were 95 to 99% higher than downwind differential concentrations, we would not consider dairy operations as significant sources of CO_2. Due to small differential concentrations and large variations in animal emissions and management techniques, seasonal trends in CO_2 and CH_4 fluctuation from dairy operations may not be easily predictable.

Nitrous oxide at Dairy 1 had the highest concentration in the winter, while Dairy 2 concentrations were highest in the summer (Table 5.3), but neither showed any significant seasonal differences. Similar to other studies (Jungbluth et al., 2001; Kulling et al., 2001), we found that N_2O concentrations downwind of the dairies were very low (less than 21 $\mu g\ m^{-3}$ for either dairy). Differential concentrations were less than 3% of upwind values, and some seasons had negative N_2O concentration differentials that were effectively zero (undetectable, given measurement error). Low concentrations coupled with short sampling periods likely contributed to a lack of seasonal differentiation for N_2O.

Nitric acid concentration from Dairy 1 was highest in the fall and winter months, and negative in the hotter summer months (Table 5.3). For Dairy 2, HNO_3 was significantly different ($P = 0.01$) among seasons with highest concentrations in the summer months, and lowest concentration in the spring, an opposite trend to Dairy 1. However, the variability by season at each dairy, coupled with the large standard errors, and low concentrations makes analysis of a significant pattern at either dairy difficult. For instance, the high concentrations detected during the summer at Dairy 2 could be an artifact from the volatilization of ammonium nitrate particulates collected on the preceding Teflon filter. Karakas and Tuncel (1997) found a similar artifact for gas-phase HNO_3 when nitrate volatilized from ammonium nitrate particulates collected on a Teflon filter, erroneously increasing the concentration of HNO_3 measurements. In turn, this can also cause NH_4^+ particulate concentrations on the Teflon filter to be lower than actual values due to volatilization of HNO_3 from particulates (Park et al., 2004), which in this case was negative. Karakas and Tuncel (1997) found that this sampling artifact was particularly evident during hot summer months with low humidity, similar to our sampling conditions. Differential HNO_3 concentrations during summer (Dairy 1) and spring (Dairy 2) were negative, indicating consumption of HNO_3 at the dairy, likely as ammonium nitrate particulates. However, NH_4^+ seasonal concentrations did not show a complementary trend. Instead, Dairy 1 had the highest concentrations in the spring, but when standard errors were taken into account, no difference in concentration was seen between seasons. Dairy 2 had the highest NH_4^+ concentration in the winter, while summer and spring concentrations were negative indicating that the cooler months favored NH_4^+ particulate formation at Dairy 2.

Due to short sampling times and low concentrations, seasonal trends were difficult to determine for HNO_3 and NH_4^+. However, NH_3 did follow expected species behaviors for changes with ambient temperature. Numerous studies have reported a seasonal cycle in NH_3 concentrations, with the highest emissions reported in the hot summer months (Aneja et al., 2000; Robarge et al., 2002; Walker et al., 2004, 2006). A study conducted by Robarge et al. (2002) showed that concentration of NH_4^+ emissions follows a seasonal pattern similar to NH_3; however, the current study showed that NH_4^+ concentrations did not vary with season. Other studies (Parmer et al., 2001; Walker et al., 2006), have found that NH_4^+ concentrations increased with decreasing temperature and low relative humidity, which favored the formation of particulates (i.e. ammonium nitrate) in the cooler months rather than the hotter ones. This is due in part to the temperature dependence of the gas to particle partitioning between NH_3 and NH_4^+ which favors the

NH_3 gas phase at hotter temperatures, and NH_4^+ particulates at cooler temperatures (Finlayson-Pitts and Pitts, 2000). In fact, at Dairy 2 negative differential NH_4^+ values were measured in the warmer months indicating that no NH_4^+ particulates were being formed in close proximity to the dairy, and/or that trapped particulates may have dissociated in the filter system and been recorded as NH_3 and HNO_3. Walker et al. (2004) reported similar results to ours, observing a minimum NH_4^+ concentration in the warmer months. They surmised that this was because NH_3 will stay in the gas phase at sites were NH_3 levels are high, such as agricultural areas, and the partitioning to NH_4^+ will be insignificant. Relative differences between downwind NH_4^+ and NH_3 show that NH_4^+ concentration was less than 1% of NH_3 concentrations measured (Table 5.3). Since NH_3 is produced in high concentrations, the formation of NH_4^+ particulates is dependent on the concentration of acidic species (i.e. HNO_3) in background air, which was also relatively low compared to NH_3 concentrations on-farm (< 0.5%). The relatively small increase of NH_4^+ particulates observed may be the result of the close sampling proximity to the dairy (less than 200 m). We surmise that NH_3 doesn't have sufficient time to react with HNO_3 to create NH_4^+ particulates in this situation. A positive differential in HNO_3 also confirms this. In some seasons the HNO_3 differential is negative indicating complete consumption with NH_3, but in most cases it is positive showing that HNO_3 is still being introduced from background air, a sampling artifact is present, or there is a source of HNO_3 on farm. Since there are minimal sources of HNO_3 formation on the dairy (some possible from NOx species produced during incomplete denitrification in anaerobic lagoons), we assume all HNO_3 is from background sources with possible enrichment in our measurements due to disassociation of particulates from the Teflon filters.

Interactions. A significant ($P < 0.01$) interaction between season and the location of the sampling station was found at Dairy 2 for N_2O, HNO_3, and NH_4^+, indicating that emission sources and sinks at the dairy had significant link to seasonal variations. Individual sampling dates among seasons (data not shown) show that due to differences in seasonal wind directions, the location of sampling systems varied with each season. For example, during the summer sampling at Dairy 2, which is also the season of highest N_2O emissions, sampling stations 1 and 2 were set-up just downwind of a small pasture pen and the composting area, both primary N_2O emission sources (Kulling et al., 2001). During this sampling period, these two locations also had the highest N_2O concentrations. During one of the winter sampling periods, when sampling stations were set up on the other side of the dairy with station 1 and 2 downwind of the drylots, the lowest N_2O concentrations were measured. While the interaction was not significant, similar examples were also found at Dairy 1 when seasonal wind direction dictated whether sampling stations were setup next to or away from primary emission sources of N_2O. The season by location interaction for HNO_3 and NH_4^+ is not as clear, and a significant value may have been found due to the large variation in concentrations rather than an actual interaction.

Vertical profile. Vertical profile patterns for each of the species measured were different at each dairy (Figure 5.3 and 5.4). At Dairy 1, peak concentrations for all species except NH_4^+ were found at ground level (Table 5.4), reflecting a strong local source emission. At Dairy 2, all compounds had multiple peaks at varying heights (Table 5.4), possibly showing the variation of vertical profile with distance from a source. Nitric acid concentrations at Dairy 2 revealed a significant difference ($P < 0.001$) within the vertical profile, but no clear pattern was identified. Carbon dioxide also had a significantly varying ($P = 0.04$) profile with height at Dairy 2.

At both dairies, NH_3 had a relatively consistent vertical profile (Dairy 1, $P = 0.04$; Dairy 2, $P = 0.02$), with a maximum concentration at the lowest sample height (2 m), then steadily decreasing concentrations with height above that. Similar results have been reported by both Erisman et al. (1988) and ApSimon et al. (1994) who also found that NH_3 emissions were highest at ground level and decreased consistently and markedly in the atmosphere with height. In this study, only concentrations up to 35 m were measured, but concentrations were still well above background levels (80% higher) at that height indicating that NH_3 emission profiles probably extend quite a bit farther up into the atmosphere. The regression relationship between ammonia and height was examined for each dairy. Dairy 1 was found to have a strong exponential relationship ($r^2 = 0.97$; $P = 0.01$), while Dairy 2 also had a strong exponential relationship ($r^2 = 0.85$), it was not significant ($P = 0.08$). This relationship of decreasing concentration with increasing height is likely due to the increase in mixing with elevation which produces a similar profile to a Gaussian distribution. Based on this exponential relationship, the maximum average height at which NH_3 would reach background levels at Dairy 1 was 62 m, and for Dairy 2 it was 125 m. The difference in maximum height between dairies is likely due to the initial NH_3 surface concentrations, which were higher at Dairy 2, as well as the measured distance from the source, which was further at Dairy 2. Other studies have found similar exponential profiles for NH_3 with concentrations above background levels up to 75 m (ApSimon et al., 1994) and 200 m (Erisman et al., 1988). The exponential decrease with height could be due to the high concentrations emitted at ground level that significantly decrease with height due to vertical mixing and transport (ApSimon et al., 1994). These considerations are important when monitoring NH_3 concentrations at a fixed height because underestimation of total concentration could be made.

Additionally, we found a seasonal influence on NH_3 concentration profiles, primarily at Dairy 2 (Figure 5.3 and 5.4). During both of the warmer seasons (summer and spring), NH_3 concentration had a second peak at 20 m. In the warmer seasons, sampling was conducted on the north side of the dairy near drylot 1 (Figure 5.2), which would contribute to the elevated concentrations seen at 2 m. The additional peak at 20 m could have been contributed by drylot 2, which was approximately 0.5 km across the dairy from drylot 1 and the sampling station. The 9 m tall milking parlor in between the two drylots could have aided in lifting the plume and producing the secondary peak (Flesch et al., 2005). During the winter season, sampling was conducted on the NE side of the dairy, and no additional peak at 20 m was seen. Ammonia concentrations at Dairy 1 had a more consistent vertical profile likely because no large building obstructions between sources or major multiple sources existed.

The vertical profiles of both NH_4^+ and HNO_3 did not reveal patterns at either dairy. Ammonium and HNO_3 concentrations have been shown to vary little with heights up to 200 m (Erisman et al., 1988; ApSimon et al., 1994). Measurements by Erisman et al. (1988) show that NH_4^+ concentration varied by only 25% between 2 and 200 m. ApSimon et al. (1994) modeled the concentration profile of HNO_3 and found that concentrations decreased sharply at ground level due to high surface deposition velocity, but above 25 m, were stable, varying by only 1 to 2 $\mu g\ m^{-3}$ up to 200 m. A lack of consistent profiles in our study for either species could have been due to the short sample times (one hour), which didn't allow a sufficient amount of either species to be collected to draw any substantial conclusions regarding vertical distribution. Additionally, as mentioned previously, the distance between major NH_3 sources and collection stations for NH_4^+ particulates may not have been sufficient to allow particulate formation to occur over the dairy site. Longer sampling times may aid in producing vertical profiles with more consistent patterns, but would risk NH_3 breakthrough of the filters.

The greenhouse gases (CO_2, CH_4, and N_2O) had profiles similar to each other in the summer months at each dairy, but greenhouse gases were not different between the two dairies ($P > 0.68$). Dairy 1 showed a very similar vertical profile and ratio of concentrations between heights for CO_2 and CH_4 (Table 5.4), indicating that primary emissions were probably from the same sources. However, Dairy 2 showed less similarity between the two profiles, possibly due to more scattered emission sources from CO_2 and CH_4 (Figure 5.4). Dairy 1 had a concentration of cows in one location in barns, while Dairy 2 had a more disperse distribution of cows over two large drylots. Since primary emissions of CO_2 and CH_4 come directly from cattle, this difference could have a significant effect in this case. Additionally, the surface area of Dairy 2 was much larger, creating a more disperse distribution of area sources and resulting in profiles with multiple emission peaks. Studies evaluating vertical profiles of greenhouse gases above 10 m were not available, so comparison to other profiles is not possible. In general, due to the low reactivity of greenhouse gases and increased mixing with height, relatively consistent vertical profiles were expected. However, data showed non-linear, varying profiles with increasing concentrations above 20 m in many seasons (Figure 5.3 and 5.4), especially for CH_4. This could be due to variations in distance from major source emissions such as composting areas and barns or drylots with season. The more distant the sampling station is from the source, the higher up the emissions should be detected. For example, NH_3 emissions had double peaks when sampling stations were in specific downwind orientation to emission sources. While they showed a slightly similar pattern, vertical profiles for each season at each dairy for N_2O were even less predictable as a function of height than CO_2 and CH_4, likely due to the low concentrations detected.

Diurnal variation. No significant diurnal patterns were identified for any of the gases measured, nor were diurnal trends similar between dairies. This is due in part to uncontrollable weather conditions which precluded a third daily sample from being collected on some sample days. This lack of data makes the identification of diurnal patterns difficult. Additionally, the time of day at which samples were taken was not identical for each sampling day due to changes in wind speed and wind direction which altered sampling time.

CONCLUSION

Our results indicate that concentrations of NH_3, NH_4^+, HNO_3, CH_4, CO_2, and N_2O from dairy systems have seasonal, vertical, and horizontal variation. Measurements made over a seasonal basis at two different dairies show that while seasonal profiles may be similar, mean concentrations and vertical profiles of gases are very variable between operations. This variation is likely due to differences in metrological conditions, type of operation (drylot vs. freestall), animal and manure management techniques, and dairy layout. Spatial and vertical profiles showed that the location and the height of measurement greatly influenced the concentration measured for all species, and that both were influenced by seasonal wind direction patterns. Also, while the majority of gases had the highest concentration below 10 m, NH_3 was the only gas that exhibited a consistent decreasing profile with height. Additionally, our vertical measurements showed that significant concentrations were still present at 35 m for all of the species. There is a need to measure gases from dairy operations on a spatial and vertical basis to better characterize total emissions and help aid in profile modeling efforts. While concentration profiles are variable with season and height, additional sampling at more locations and seasons will help in recognizing clear patterns in profiles and aid in better understanding of emission profiles from dairy operations. This is essential for future quantification and characterization of emission plumes for both regulation and modeling purposes.

Table 5.1. Least squares means and standard errors (in parentheses) for meteorological data by season for Dairy 1 and Dairy 2 averaged over height.

Season	Month	Pressure	Temperature	Relative Humidity	Wind Speed	Wind Direction
		mbar	°C	%	m s^{-1}	°
Dairy 1†						
Summer	September	845.7 (0.43)	22.94 (0.44) a	39.9 (1.5)	2.76 (0.43)	195.9 (11.1)
Fall	Oct./Nov.	838.1 (0.52)	10.93 (0.56) b	24.3 (1.2)	3.01 (0.13)	175.7 (8.5)
Winter	January	833.6 (0.50)	5.39 (0.54) c	21.2 (0.5)	2.78 (0.25)	163.5 (3.7)
Spring	May	810.8 (0.40)	21.58 (0.46) a	19.42 (0.9)	3.48 (0.24)	171.4 (2.3)
Dairy 2						
Summer	August	848.2 (0.40)	29.67 (1.25) a	16.1 (2.5)	2.45 (0.27)	160.2 (5.3)
Fall‡	NA	-	-	-	-	-
Winter	January	845.2 (0.65)	6.62 (0.67) b	24.6 (1.8)	2.56 (0.53)	179.8 (17.5)
Spring	May	854.1 (0.72)	9.75 (1.01) c	23.7 (4.1)	3.41 (0.17)	258.1 (4.5)

†Different letters, a, b, c, denote significant differences for an alpha level of 0.05.

‡ Data not available.

Table 5.2. Upwind seasonal concentration least squares means and standard errors (in parentheses) for Dairy 1 and Dairy 2 averaged over height, sampling location, and seasonal sampling dates.

Season	CO_2	CH_4	N_2O	HNO_3	NH_3	NH_4^+
	mg m^{-3}	µg m^{-3}				
Local/Global background†	584.6	*1043*	*516.7*	*NA*	*NA*	*NA*
Dairy 1 seasonal upwind, avg‡						
Summer	621.92 (5.72)	1084.1 (3.1)	550.2 (4.4)	2.45 (0.17)	8.81 (1.24)	0.75 (0.03)b
Fall	622.07 (8.31)	1066.7 (2.3)	557.1 (1.9)	2.84 (0.32)	9.77 (1.54)	0.26 (0.01)c
Winter	624.74 (1.53)	1075.1 (18.3)	535.5 (2.4)	0.14 (0.01)	12.56 (0.13)	1.18 (0.01)a
Spring	614.92 (2.69)	1032.5 (4.3)	506.4 (1.5)	0.12 (0.04)	10.35 (1.2)	0.06 (0.03)c
Dairy 2 seasonal upwind, avg						
Summer	641.82 (8.53)	1135.7 (17.9)	560.4 (13.3)	0.72 (0.24)b	20.30 (4.35)	0.70 (0.05)
Fall§	-	-	-	-	-	-
Winter	617.90 (3.37)	1268.3 (26.3)	542.0 (1.9)	0.44 (0.03)b	22.51 (1.78)	0.66 (0.06)
Spring	627.22 (2.29)	1077.2 (2.5)	519.6 (1.2)	3.62 (0.28)a	33.84 (4.46)	0.44 (0.05)

†Global data (CO_2, CH_4, and N_2O) from Godish (2004) and CDIAC (2006); µg m^{-3} concentration calculated at 15° C and 84.3 kPa. Local data not available (NA).

‡Different letters, a, b, c, denote significant differences ($P < 0.05$).

§Data not available.

Table 5.3. Downwind seasonal differential concentration least squares means and standard errors (in parentheses) for Dairy 1 and Dairy 2 averaged over height, sampling location, and seasonal sampling dates.

Season	CO_2	CH_4	N_2O	HNO_3	NH_3	NH_4^+
	mg m^{-3}	µg m^{-3}				
Dairy 1 seasonal downwind, avg†						
Summer	9.26 (3.68) ab	123.1 (20.1)	10.62 (2.55)	-0.84 (0.15)	122.8 (33.5)	0.15 (0.09)
Fall	3.78 (1.37) b	179.9 (27.1)	4.24 (1.24)	0.63 (0.45)	74.7 (13.3)	0.15 (0.04)
Winter	27.27 (3.11) a	237.7 (35.3)	16.28 (2.61)	0.65 (0.05)	117.7 (23.7)	0.25 (0.06)
Spring	23.75 (4.97) a	185.1 (30.3)	5.01 (1.65)	0.01 (0.03)	164.6 (24.1)	0.33 (0.07)
Dairy 2 seasonal downwind, avg						
Summer	12.88 (3.20)	42.2 (7.9)	20.93 (5.57)	1.10 (0.25) a	393.7 (58.8)	0.58 (0.07)
Fall‡	-	-	-	-	-	-
Winter	21.84 (3.84)	197.3 (51.0)	-2.01 (1.97)	0.72 (0.10) a	166.6 (15.9)	0.03 (0.08)
Spring	16.34 (2.01)	73.9 (10.1)	6.81 (2.18)	-1.66(0.48) b	127.7 (27.4)	0.08 (0.06)

†Different letters, a, b, c, denote significant differences ($P < 0.05$).

‡ Data not available.

Table 5.4. Downwind differential least squares means and standard errors (in parentheses) for concentrations by height for Dairy 1 and Dairy 2 averaged by sampling location and seasonal sampling dates.

Height	CO_2	CH_4	N_2O	HNO_3	NH_3	NH_4^+
m	mg m^{-3}	µg m^{-3}				
Dairy 1†						
35	11.39 (3.38)	164.4 (28.8)	6.84 (2.28)	0.25 (0.34)	27.0 (3.8)c	0.22 (0.06)
20	9.00 (2.87)	139.7 (26.1)	6.99 (1.96)	0.59 (0.65)	54.8 (8.0)c	0.23 (0.07)
10	13.25 (4.51)	199.9 (39.6)	5.67 (2.64)	-0.76 (0.25)	100.7 (16.8)b	0.17 (0.07)
5	12.63 (3.56)	179.8 (35.3)	8.33 (1.99)	0.40 (0.41)	154.3 (28.4)ab	0.20 (0.05)
2	16.46 (3.38)	213.3 (39.1)	10.80 (2.13)	0.66 (0.53)	194.7 (34.1)a	0.18 (0.07)
Dairy 2						
35	12.17 (3.71)a	122.2 (53.2)	6.61 (6.13)	0.44 (0.39)ab	109.6 (23.4)b	0.27 (0.12)
20	13.81 (3.47)ab	105.8 (43.9)	7.91 (6.00)	0.76 (0.39)a	222.9 (42. 5)ab	0.25 (0.10)
10	23.84 (4.30)b	111.5 (42.0)	9.51 (5.50)	0.07 (0.54)bc	205.5 (28.5) a	0.18 (0.13)
5	22.42 (5.66)b	111.8 (44.6)	11.92 (5.23)	0.26 (0.44)c	274.9 (57.9)a	0.16 (0.10)
2	12.93 (3.99)ab	95.9 (44.1)	8.46 (4.92)	0.32 (0.36)abc	399.7 (95.7)a	0.27 (0.09)

†Different letters, a, b, c, denote significant differences ($P < 0.05$).

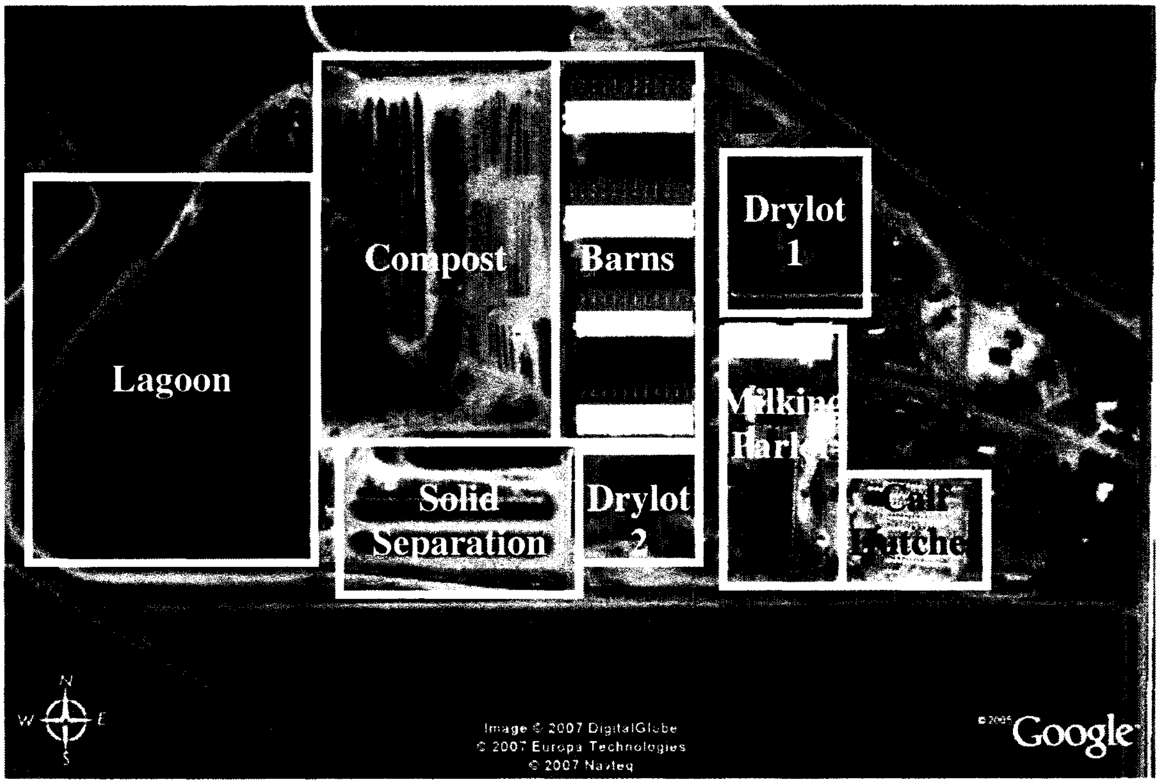

Figure 5.1. Layout of Dairy 1. Boxes represent major areas of emissions on the operation. One inch = 0.11 km. (Image acquired from Google Earth).

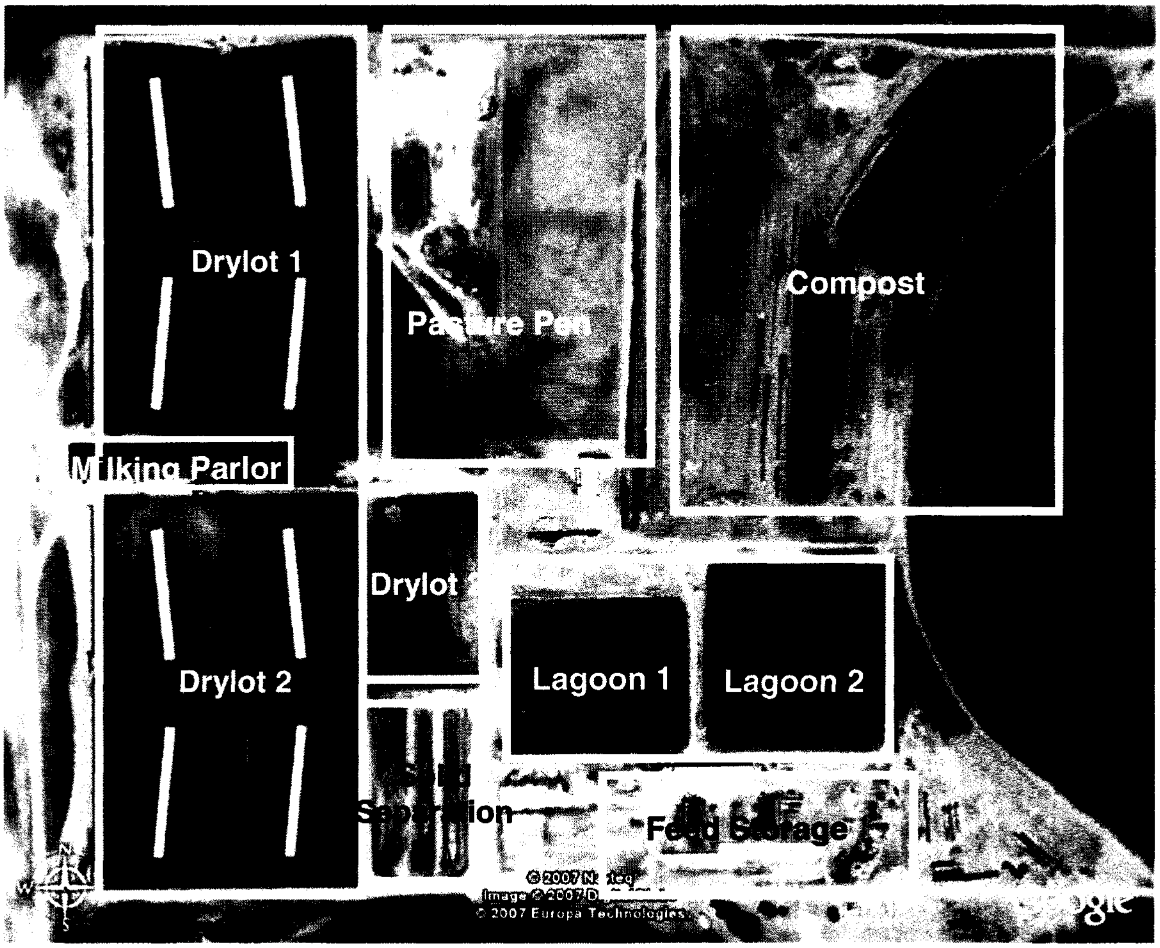

Figure 5.2. Layout of Dairy 2. Boxes represent major areas of emissions on the operation. One inch = 0.16 km. (Image acquired from Google Earth).

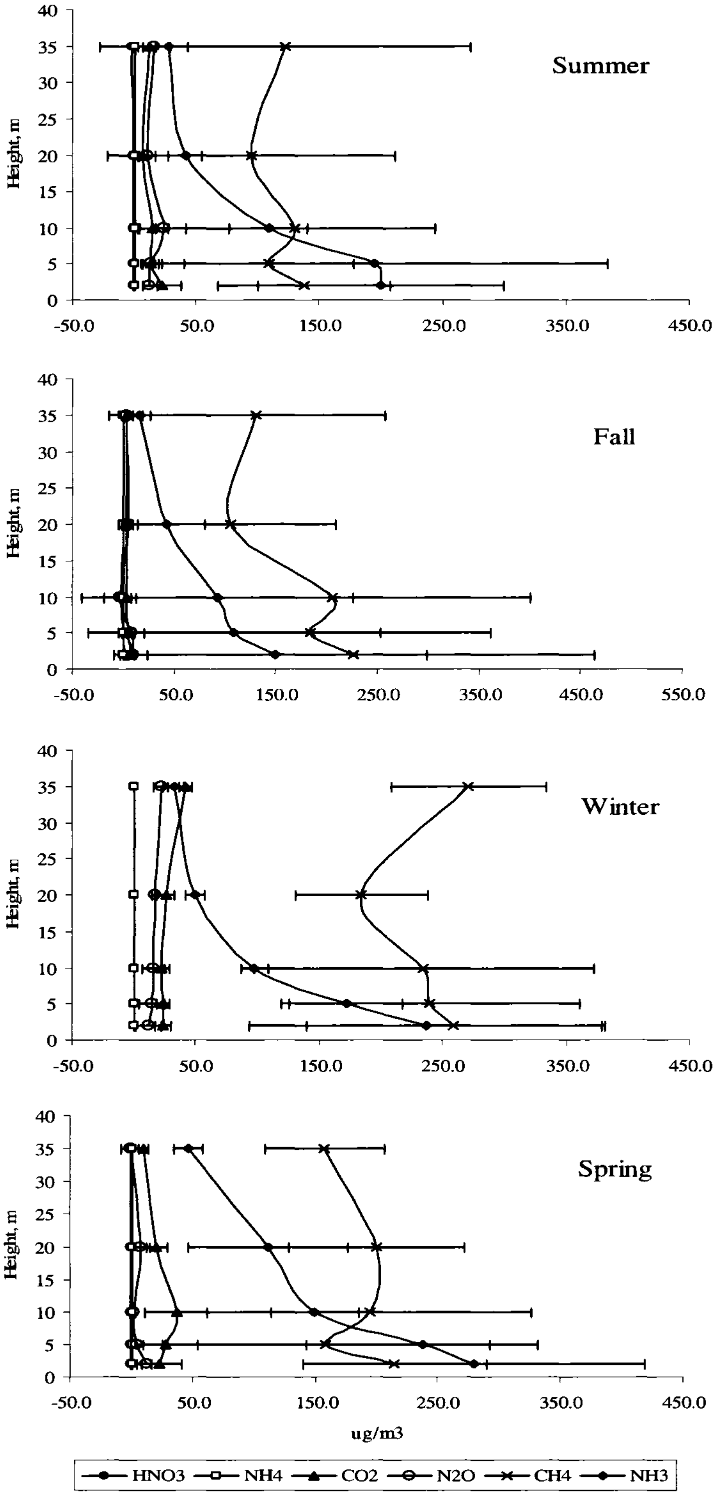

Figure 5.3. Trace gas and particulate enrichment in the atmospheric boundary layer downwind of Dairy 1. Seasonal profiles for ammonium (NH_4^+), nitric acid (HNO_3), nitrous oxide (N_2O), methane (CH_4), and ammonia (NH_3) are in $\mu g\ m^{-3}$, carbon dioxide (CO_2) is in mg m^{-3} to allow all profiles to be shown on the same figure. Positive values indicate enrichment.

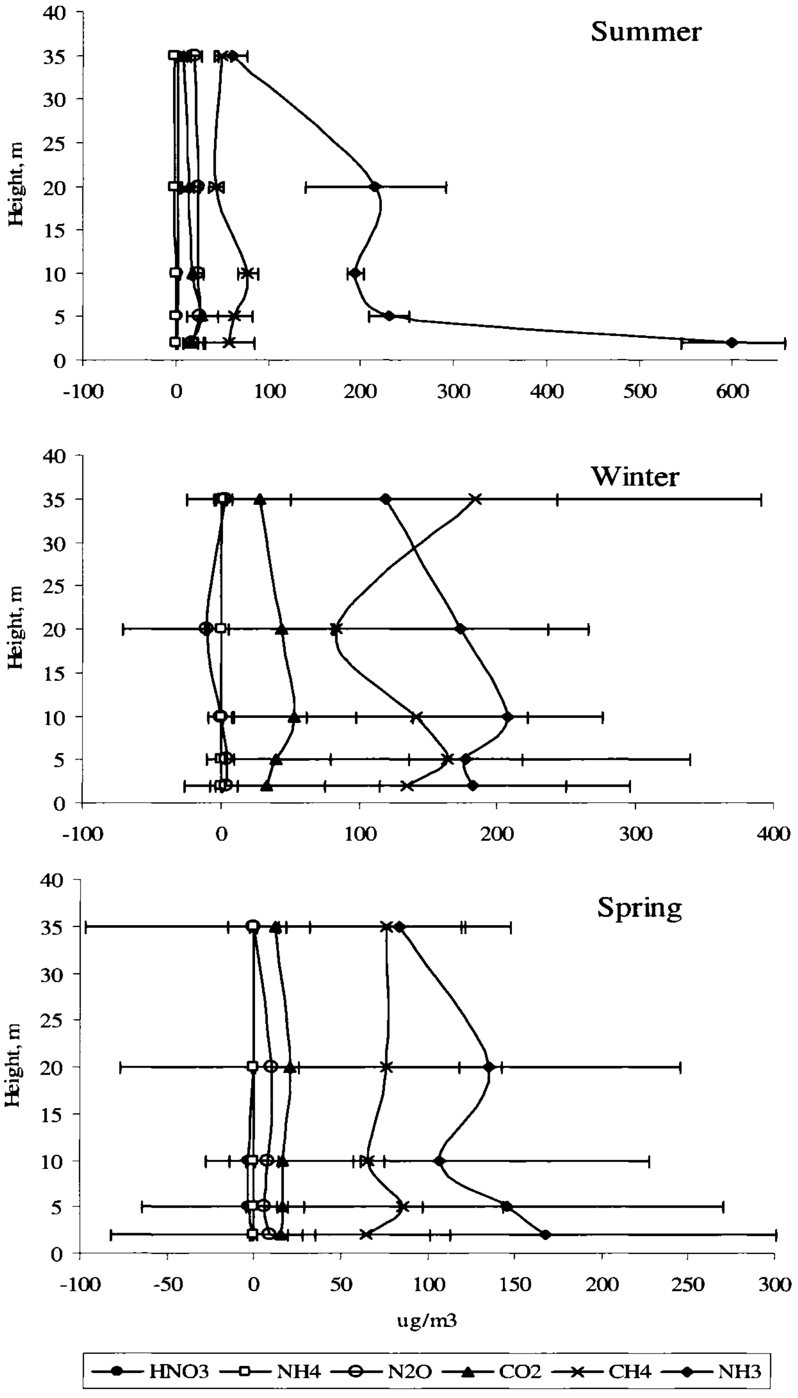

Figure 5.4. Trace gas and particulate enrichment in the atmospheric boundary layer downwind of Dairy 2. Seasonal profiles for ammonium (NH_4^+), nitric acid (HNO_3), nitrous oxide (N_2O), methane (CH_4), and ammonia (NH_3) are in $\mu g\ m^{-3}$, carbon dioxide (CO_2) is in mg m^{-3} to allow all profiles to be shown on the same figure. There is no fall data to report for Dairy 2. Positive values indicate enrichment.

CHAPTER VI

CRITICAL EVALUATION OF THE SYSTEM METHODOLOGY DEVELOPED AND FUTURE RESEARCH DIRECTIONS

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DISCUSSION OF SYSTEM METHODOLOGY

The novel system, developed and described in Chapter IV (this dissertation), has some unique attributes and benefits, but also some challenges. After testing the equipment and using the system in the field, a critical evaluation was put together for future users.

Benefits

The system has many benefits demonstrated in Chapter V (this dissertation). Unlike any currently available methodologies for measuring gaseous emissions from livestock operations, our system allows a user to monitor emissions from an entire operation, while also evaluating its parts. We found that an average of the three sample locations gave an average emission concentration from each operation, but we could also look at each individual sampling station and evaluate the concentration profile from a source. Not many other systems allow this flexibility. The addition of extra sampling stations in the field could help further characterize the plume and better evaluate on-farm sources.

The most prominent feature of the system is the ability to measure vertical profiles of concentrations. While we only evaluated profiles up to 35 m, the current system set-up allows for vertical measurement up to 200 m. Measurement above this height is not practical due to constraints associated with tubing length and lift weight limits of the balloons (max 14 kg).

Another benefit of the system is its mobility. This feature allows the system to be set up on any type of operation under any field conditions. The mobility also allows for adjustment of sampling locations with changing wind directions.

Challenges

The system works well under ideal weather conditions (clear skies, 4 to 6 m s^{-1} winds, consistent wind direction, mild temperatures, etc.), but is limited in harsher weather; and ideal weather conditions are rare in Colorado during any season.

We lost a few balloons due to turbulent winds and downdrafts. The system was modified with stronger tether lines and clips to prevent losses due to line breakage, but balloon touchdowns due to downdrafts were still destructive and only preventable with abortion of the sampling event and complete deflation of the balloons. Once the system was completely taken down, cost restrictions (i.e., helium gas) prevented us from launching it again for a second day of sampling, thus limiting our field replications. Additionally, any precipitation was equally destructive as moisture created holes in the balloon material within a few days of storage. High winds (greater than 9 m s^{-1}) were able to lift the balloon and winch, possibly damaging the winch and sampling equipment on the line. Due to the high costs of all of this equipment, any conditions which could cause damage to the system were avoided. This forced us to abort many sampling periods (e.g., times, days, and seasons) to avoid equipment losses. If balloons could be tethered safely to the ground and covered, this would help reduce the need for total disassembly of the system and deflation of the balloons during brief periods of poor weather. Additionally, the ability to only sample under ideal conditions may bias the data collected. Sampling under more challenging conditions (i.e., high winds, rain), may lend interesting data that we are not be able to collect with this system.

The most prominent challenge to the system was changing wind directions. Our sampling methodology relies on a consistent wind direction throughout the sampling period. If the wind direction shifted during a sampling period, sampling times had to be shortened, or stopped and restarted. The sampling times used were already shortened to one hour to help ensure a consistent wind direction throughout the sampling time. However, when we did this, we sacrificed the collection of species found in low concentrations in background and on-farm plumes, thus contributing to our insignificant findings for species such as nitric acid, ammonium, and nitrous oxide. Longer sample times (maximum of 2 hours to avoid ammonia breakthrough on the filters) would have allowed a more sufficient collection of these species and might have helped clarify some of their seasonal and vertical patterns. The mobility of the system helped alleviate some of these problems, allowing us to move with changing winds, but this was not always easy. When the winds did shift, it was a slow process, taking anywhere from 45 minutes to over an hour. During this time, samplers are subject to contamination if left on the tether lines. We found the best option was to take the sampling equipment down if sampling had been conducted for over 30 minutes prior to wind change. This caused concentrations to be below detection limits for some species (nitric acid and ammonium), but salvaged the sample period.

Additional challenges were the need for adequate numbers of personnel to operate the stations in addition to operation and equipment costs. A minimum of one trained operator should be present at each sampling station, but two people at each station was optimal. Because the weather had such a large influence on our ability to sample, our sample days were relatively spontaneous within a set window of two weeks within a season. We found it was difficult to maintain trained personnel under these conditions, but there is little that can be done about this. Another inherent challenge was the operational cost of the system. Each field sampling date required helium to inflate the balloons, personnel costs, gas and travel time, and sample analysis expenses. If any equipment had to be replaced, the costs were sufficiently higher. However, all of these costs were unavoidable, and the system was put together using the best equipment for the lowest price.

Future Methodology Recommendations

Recommendations can be made to improve the system in the future to obtain the best data and minimize sampling errors. These recommendations are mainly associated with reducing errors within the sampling equipment and improving analysis of the collected data.

When the system was developed, we thought that having three samplers at the upwind station instead of five, like the downwind stations, would save on analysis costs and equipment purchases. However, upon analysis of the data, we found that the extra two heights would have lent some vital concentration data to our analyses. For instance, the extrapolated averages of the 35 and 10 m, and 10 and 2 m samples were used to predict the concentrations at 20 and 5 m. When we looked at the downwind vertical profiles we often saw spikes in concentration at these two heights (20 and 5 m). It is possible that this is a coincidence; however, the lack of true concentration measures might have contributed to the inconsistency of the vertical downwind differential (downwind minus upwind) profiles. In the future, five samplers should be placed at the upwind station.

Another future consideration is validation of the syringe pumps. We did not validate them prior to use in the field, as we thought it was unnecessary. However, variable vertical greenhouse gas (carbon dioxide, methane, and nitrous oxide) data suggests that they should be validated for collection efficiency. This could be done easily in a laboratory setting by releasing a known concentration of methane gas and collecting it in a set interval into the syringe pumps. This would demonstrate if there were any leaks in the system, or contamination from the vacuum pumps. Additionally, on a larger scale, a tracer gas trial could be conducted to evaluate the collection efficiency of the entire system under field conditions. A tracer gas (i.e., SF_6) could be released from various locations within the dairy while the system is running, allowing us to evaluate the efficiency of collection at each of the sample locations. This would also aid in clarifying any changes in vertical profiles contributed by turbulent forces (i.e., buildings, obstructions) acting on emissions from sources.

Lastly, further analysis of the concentration data needs to be done to determine source flux to begin to model emissions. If source flux is known, a mass balance approach could be used to determine the flow of nutrients through a dairy operation. Preliminary flux analysis shows that only ammonia has a predictable source and profile, so this may be the best place to start. Balance between input (i.e., feed) and output (i.e., manure, milk, and meat) could help to quantify the percentage of nitrogen that is actually volatilized as ammonia from dairy operations. Further work in this area needs to be done.

Additional sampling at more dairy operations also needs to be done to help clarify seasonal and vertical patterns we observed. There is so much variation between operations that a larger sample size is needed to account for this variation in order to make larger inferences about dairy operations with our data. More sampling days per season would increase replication and decrease error within season.

Overall, the system has potential to produce very novel and useful data, but first, some design and operational changes need to be made based on the recommendations above. With these changes, this system will aid in modeling and research efforts to better characterize emissions from livestock operations.

FUTURE RESEARCH QUESTIONS

The future of animal agriculture is based upon consumer choices and environmental and economic sustainability. Consumers have the ability to make changes in the animal agriculture industry based on what they do and do not buy. Educated consumers are starting to make more environmentally based choices, such as buying organic or free-range meats and produce, or products from specific operations that have shown a commitment to reducing their environmental impact. These choices shape the future direction of animal agriculture.

From an environmental perspective, air quality is becoming a more common topic in social circles. Global warming, the most prominent topic of concern, has spurred consumers to make choices that reduce their global impact. Consumers are becoming aware of the emission of methane from agriculture, and are possibly choosing against animal products as a result. In Colorado, nitrogen deposition and reduced visibility in Rocky Mountain National Park has forced scientists as well as the public to become educated about nitrogen species and identifying sources of excess atmospheric nitrogen. The finger is being pointed at animal agriculture due to the high emission of ammonia from confinement animal feeding operations. Again, educated consumers can choose to select against operations that don't address their nitrogen emissions and environmental impacts, or can choose not to consume animal products at all. In this light, I would say that the most important question for animal agriculture is: How are we going to make confinement animal feeding operations more sustainable and reduce their environmental impact? If this question is not answered, then the future of animal agriculture, and its impact on the environment, could be bleak. Additionally, specific to air quality, I would ask: How can we reduce air emissions while still maintaining animal production and not imparting the problems onto other links within the system (i.e., water, soil, etc.)? And, how can this be done in an economically feasible way for producers?

Unless Americans are willing to pay the true price for their food, which reflects the environmental, social, and health impacts of production, farmers will have to absorb the costs associated with mitigation of emissions. If technologies and practices to reduce emissions are not cost effective, they will likely not be adopted on a voluntary basis. Instead, reductions in air emissions from animal operations will have to be accomplished with regulations and other means of enforcement. So, what unique technologies can be created that modify the current system in a positive way?

Additionally, like consumers, producers need to be educated about where their emissions come from, why they occur, and how they can do something about it. Producers need to be educated so they can be proactive and let the public know that they care, and that their product is important to the sustainability of agriculture. Mahatma Gandhi said, “Be the change that you wish to see in the world.” I believe this is true for any segment of the chain from researchers, to producers, regulators, and consumers. If a small group decides to make a change in a positive direction, then eventually more people will follow. We should look to the positive examples already out there and ask, how can animal agriculture become more sustainable, and how are we going to get there using current models and outside-of-the-box thinking? It is time to implement solutions that give animal agriculture a new positive impact on the environment, especially on air quality.

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