

A REVIEW OF AMMONIA EMISSIONS MITIGATION TECHNIQUES FOR CONCENTRATED ANIMAL FEEDING OPERATIONS

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INTRODUCTION

Several approaches have been suggested and evaluated for reducing ammonia emissions from excreted animal manure; reduction of nitrogen excretion through dietary manipulation, reduction of volatile ammonia in the manure to stop ammonia loss, and segregation of urine from feces to reduce or stop contact of urease and urine. When urine-feces segregation is not an option, urease inhibitors can be used to reduce or eliminate the hydrolysis of urea into ammonia. Methods for reducing volatile ammonia in manure include the reduction of pH, which shifts the equilibrium balance in favor of ammonium over ammonia, use of other chemical additives that bind ammonium-N, and use of biological nitrification-denitrification to convert ammonium into other N-species such as nitrite, nitrate, or gaseous nitrogen. Other methods for mitigating ammonia emissions target emitting surfaces, and include capturing (using physical covers) and treating captured air to remove ammonia (using biofilters or biocovers, and scrubbers), and direct manure injection or incorporation into the soil. Manure collection facility designs and appropriate facility management are also essential for abating ammonia emissions. This article provides a review of these approaches in the context of concentrated animal feeding operations.

MITIGATION MECHANISM:

Ammonia emitted from concentrated animal feeding operations (CAFOs) may soon be subjected to state and federal regulations aimed at protecting air resources when data for estimating emissions to the atmosphere from CAFOs have been collected from an ongoing National Air Emission Monitoring Study (NAEMS). This NAEMS is funded by the Agricultural Air Research Council, a non-profit organization that receives its funds from livestock industry groups, and is being overseen by the EPA Office of Air Quality Planning and Standards. Thus there is a need to identify as well as develop practices and technologies to assist producers to prevent or mitigate ammonia emissions, not only for CAFOs to meet regulations requirements but also for livestock producers to be good environmental stewards.

Ammonia volatilization is one of the pathways for N loss from animal feeding operations. Ammonia volatilization is a critical issue because it represents a loss of fertilizer value and can adversely impact the environment (McGinn and Janzen, 1998). Ammonia can also be deposited from the atmosphere and may be beneficial to plants as a nutrient (N) source for growth. Conversely, when excess N is deposited in N-sensitive ecosystems, the N may impact these systems negatively. Potential consequences associated with exceeding threshold concentrations of both oxidized and reduced forms of N in the environment include: (1) respiratory diseases caused by exposure to high concentrations of fine particulate aerosols (PM_{2.5}); (2) nitrate contamination of drinking water; (3) eutrophication of surface water bodies resulting in harmful algal blooms and decreased water quality; (4) vegetation or ecosystem changes due to higher concentrations of N; (5) climatic changes associated with increases in nitrous oxide (N₂O); (6) N saturation of forest soils; and (7) soil acidification through nitrification and leaching (Kirchmann et al., 1998; Kurvits and Marta, 1998; Jongbloed et al., 1999).

The objective of this paper is to review the state of the science on the mitigation of ammonia from animal feeding operations with a view of summarizing the information on the effectiveness of current mitigation strategies on the reduction of ammonia emission. Strategies for reducing NH₃ losses from CAFOs (Table 1) are directed towards reducing: (1) NH₃ or NH₄⁺ formation or production, (2) NH₃ losses after it has been formed, and (3) volatile N species. Some specific potential control strategies for NH₃ control from animal production facilities include changes in diet, barn design or retrofits, cleaning building exhaust air, manure treatment methods, and land application techniques. In practice, to obtain adequate NH₃ volatilization abatement in animal production operations a combination of these control strategies are used.

Table 1 - Summary of ammonia abatement strategies in concentrated animal feeding operations

Control Practice	Source or Location			
	Excreted Manure and Urine	Confinement Facilities	Treatment & Storage	Land Application
	<ul style="list-style-type: none"> • Reduce N excreted by reduced protein diets or improved balance of amino acids. • Dietary electrolyte balance, affecting urinary pH. 	<ul style="list-style-type: none"> • Minimize emitting surface area. • Remove manure frequently (belt transport, scrape, or flush). • Filter exhaust air (bioscrubbers, biofilters, or chemical scrubbers). • Manure amendments (acidifying compounds, organic materials, enzymes, and biological additives). 	<ul style="list-style-type: none"> • Cover to reduce emissions or collect gas. • NH₃ stripping, absorption and recovery. • Chemical precipitation e.g. struvite. • Biological nitrification (aerobic treatment). • Acidifying manure. 	<ul style="list-style-type: none"> • Injection or incorporation into soil soon after application. • Application method to reduce exposure to air (e.g. low-pressure irrigation near surface, drag or trail hoses). • Acidifying manure.

1. REDUCTION OF NITROGEN EXCRETION

Minimizing nitrogen excretion, which can be achieved through dietary-modifications, is naturally the first line of defense in curbing ammonia emissions from livestock operations (Satter et al., 2002). Available research data indicates that diets fed to animals have profound effects on ammonia emissions from excreted manure. Overfeeding dietary protein, imbalanced amino acid supply, and reduced energy availability for ruminal fermentation in ruminants result in increased urinary and fecal N losses and consequently increased ammonia emissions from manure.

In non-ruminants (for example; pigs), N excretion has been reduced by either shifting N excretion from urine to feces by increasing fiber in the feed or reducing the N content in the diet (Canh et al., 1997; Canh et al., 1998b). Reports indicate that feeding low CP diets to pigs can reduce (28-79 %) N excretion in the manure (Hobbs et al; 1996; Canh et al., 1998a). Panetta et al. (2006) reported decreased ammonia emission rates from 2.46 to 1.05 mg/min with decreasing dietary CP levels from 17.0 to 14.5%. Similarly, O'Connell et al. (2006) observed increased ammonia emissions from pig slurry from a 22 against a 16% CP in the diets. For broiler and layer chickens, reduced protein diets have resulted in reduced N excretion (Jacob et al., 2000). Thus, with some few notable exceptions (McGinn et al., 2002; Clark et al., 2005), reduction of dietary CP result in significant reduction in ammonia loss from pigs (Otto et al., 2003; Hayes et al., 2004; Velthof et al., 2005) and poultry (Ferguson et al., 1998; Nahm, 2003) operations. Other strategies such as supplementation of the diet with zeolite (Meisinger et al., 2002; Kim et al., 2005), antibiotics and probiotics (Han and Shin, 2005), vegetable oil (Leek et al., 2004), plant extracts (rich in tannins and saponins; Colina et al., 2001; Vliwisli et al., 2002), and exogenous enzymes (Smith et al., 2004; Clark et al., 2006; O'Connell et al., 2006) have been used with varied success to reduce ammonia losses from pig and cattle manure. In practice efforts to reduce ammonia emissions must be balanced with effects on animal performance in determining optimal protein concentrations and forms in the diet (Cole et al., 2005; Panetta et al., 2006).

In ruminants (cattle; for example), diet composition as well can have significant effects on urinary urea excretion and consequently ammonia losses from manure and overall efficiency of utilization of dietary N (Klopfenstein et al., 2002; Satter et al., 2002). Generally, ruminants are relatively inefficient utilizers of dietary N. The efficiency of transfer of feed N into milk protein N (MNE) is on average 24.7±0.14%, with a min and max of 13.7 and 39.8%, respectively (Hristov et al., 2004a); the remaining N being lost to the environment from urine and feces. In dairy cows, urinary N losses linearly decrease with decreasing dietary CP levels without affecting milk and milk protein yields and composition; MNE of 36% was achieved with the lowest CP diet (13.5%; Olmos Colmenero and Broderick, 2006). Cows fed 15.0 to 18.5% CP diets produced similar milk yields (32 to 39 kg/d) while simultaneously increasing N excretion and urinary N proportion (Groff and Wu, 2005). Reduction of N excretion from dairy cows can be achieved mainly by the reduction of N intake in the form of ruminally degradable protein (RDP; Kebreab et al., 2002). Utilizing a combination of prediction equations (urine volume) and actual analyses (urine composition), de Boer et al. (2002)

demonstrated the importance of the ruminal N balance (OEB) in reducing N losses in dairy cows. Increasing OEB from 0 (maximal utilization of RDP) to 1,000 g cow⁻¹ d⁻¹ resulted in linear increase in urinary N excretions. Feeding excess RDP resulted in greater ruminal ammonia and milk urea N concentrations and increased urinary N losses (by 27%; Hristov et al., 2004). Decreasing CP in diets fed to cows in mid [17 to 15% CP, ruminally undegradable protein (RUP) of 5.5 to 7.3], or late lactation (14 to 12.5% CP) can reduce the cost of the diet and waste N excreted from the cow. However, early lactating dairy cows need sufficient dietary RUP. After peak milk and DMI, CP and especially RUP requirements decline with declining milk production (Kalscheur et al., 1999). Using ruminally-protected amino acids enables an efficient use of low CP diets for production purposes. With ruminally-protected methionine (up to 25 g/d), milk yield was maintained and MNE increased from 26 to 34% as dietary CP decreased from 18.6 to 14.8% (Broderick, 2005). Methionine supply to low (13%) CP diets decreased proportion of urinary N in the total excreta N (Krober et al., 2000). Carbohydrate level and availability in the diet can also have a significant effect on ruminal ammonia utilization and consequently urinary urea output. Increasing dietary net energy of lactation concentration from 1.55 to 1.62 Mcal/kg decreased urinary urea N excretion and increased MNE (from 25 to 30%, respectively), while increasing dietary CP level from 15.1 to 18.4% had an opposite effect by increasing urinary urea N excretion and decreasing MNE (Broderick, 2003).

Dietary CP levels and effects on urinary urea excretion are directly related to ammonia emissions from cattle manure. Smits et al. (1995) fed dairy cows two diets differing in ruminally available protein (OEB; 40 vs. 1,060 g/d) and reported a significant increase in urinary urea-N concentrations and ammonia emissions from manure (by 39%) with the high-OEB diet. Külling et al. (2001) demonstrated that at 17.5% CP in the diet, N losses from manure after 7 weeks of storage were from 21 (slurry) to 108% (urine-rich slurry) greater than the N losses from manure from cows fed 12.5% CP, with respective ammonia emissions rates of 163 and 42 µg m⁻² s⁻¹. Low protein diets (13.5-14% CP) fed to dairy cows resulted in significantly lower ammonia release from manure compared with the high CP (15-19%) diets (Frank and Swensson, 2002; Frank et al., 2002). Similar results were reported for feedlot cattle (Cole et al., 2005; Todd et al., 2006). For example, decreasing CP content of finishing cattle diets from 13 to 11.5% reduced daily ammonia flux by 28% (Todd et al., 2006). In summary, reducing CP in beef cattle diets is a practical and cost-effective way to reduce ammonia emissions from feedlots.

Ammonia volatilization is directly related to the proportion of aqueous ammonia (NH₃) in the total ammoniacal-N (NH₄⁺ plus NH₃). In general, at constant temperature pH determine the equilibrium between NH₄⁺ and NH₃ with a lower pH favoring the ammonium form and hence lower potential of ammonia volatilization. Thus, low urinary pH may be a key factor for reducing ammonia emissions from cattle manure. Various dietary treatments can decrease urinary pH (Stockdale, 2005). Anionic salts (Tucker et al., 1991; Bowman et al., 2003; Mellau et al., 2004) and high fermentable carbohydrates levels (Mellau et al., 2004; Andersen et al., 2004) can reduce urinary pH to below 6.0. In non-ruminants, diet acidification with organic (benzoic) acids (Martin, 1982) or Ca and P salts (Kim et al., 2004) reduced urinary pH and ammonia emissions from pig manure (Canh et al., 1997; Canh et al., 1998a, b).

2. REDUCTION OF VOLATILE NITROGEN

Ammonia volatilization from manure is predominantly influenced by the concentrations of un-ionized NH₃-N and ionized NH₄⁺-N in solution if environmental factors are constant. Therefore, a rational way of reducing ammonia volatilization is to reduce the concentrations of these volatile N species. Five common approaches used to reduce volatile N include: urine-feces segregation, inhibition of urea hydrolysis, pH reduction, binding ammonium, and bioconversion to non-volatile N species.

Urine feces segregation

In general, surplus and inefficient utilization of crude protein or amino acids in livestock diets is the source of N in urine and feces. The majority of N (as much as 97%) is excreted in the form of urea in the urine of cows or pigs and in the forms of organic N in the feces (McCrorry and Hobbs, 2001). In a matter of hours to a few days, urea is converted to NH₄⁺-N by the enzyme urease, which is found in feces (and in the environment) but not in the urine (Beline et al., 1998). The NH₄⁺-N is subject to volatilization from manure depending on pH conditions. In contrast, the breakdown of complex organic N forms in feces occurs more slowly, requiring months or even years to complete. In both cases, N is converted to either NH₄⁺-N at low pH or NH₃-N at high pH. This is the basis of the segregation of feces and urine immediately upon excretion of either so that urease enzymes in the feces have reduced contact with the urea in urine. This concept has been tested in two ways. One method uses a conveyor-belt to separate urine and feces, with urine flowing into a pit, while feces left on the belt are conveyed into a separate collection-pit (Lachance et al., 2005; Stewart et al., 2004). The other method drains urine away from feces into a urine-pit immediately after discharge using appropriate floor designs while the feces are then scraped or washed into a separate feces pit (von Bernuth et al., 2005; Swierstra et al., 2001; Braam et al., 1997a; Braam et al., 1997b; Swierstra et al., 1995).

The efficacy of urine-feces segregation in the abatement of ammonia emissions from animal manures is summarized in Table 2. Segregation of urine from feces achieves as much as 99% reduction in ammonia emissions in laboratory studies (Panetta et al., 2004). However, pilot and full-scale urine-feces segregations have been less effective. Several researchers have evaluated a conveyor belt system (Lachance et al., 2005; Stewart et al., 2004). Lachance et al. (2005) compared the performances of three urine-feces separation systems (belt, net, V-shaped scraper) in pig grower-finisher housing. Without the separation process, removing the manure every 2-3 days significantly reduced NH₃ emissions by 46%, compared to the 8-weeks removal in the

control. Using the belt or the net and manure removal within a storage period of 2-3 days, the separation of the urine and feces directly under slats resulted in a 49% reduction of NH₃ emissions; this practice was not significantly different from not separating urine and feces. Stewart et al. (2004) also evaluated an inclined conveyor belt used directly as a dunging area in a swine barn. The average ammonia emission in this system was 47% lower than a conventional grower-finisher system with a pit plug design.

Swierstra et al. (2001) investigated pre-cast concrete floors with grooves and a manure scraper in a cow barn. The urine drained along the grooves and through perforations in the grooves spaced about 1 m apart. The perforations were opened and closed to drain urine directly into a slurry pit below and to drain urine at one end of the alley. The feces were scraped to one end of the alley. The floor system was constructed in one compartment of a mechanically ventilated experimental building, while in another compartment, a traditional slatted floor served as a control. Ammonia emissions in the test compartment with open and closed perforations were reduced by 46 and 35% compared with the control compartment.

A similar system utilizing a V-shaped pit floor with an adapted scraper installed beneath the slatted floor of swine pens was evaluated by von Bernuth et al. (2005). Feces on the pit floor slope were scraped to a collection point after the liquid, including urine, had drained to a holding tank via a central pipe. Ambient ammonia concentration did not exceed 7.5 ppm in the pens throughout the monitoring period. Braam et al. (1997a) evaluated mitigation of ammonia emission from similar V-shaped solid floors with a gutter at the bottom of the V-groove to drain urine in cow houses, with and without water spraying. Ammonia emission from the system without spraying water was reduced by 50% on average compared with a control. In addition, ammonia emission was further reduced by an average of 65% when water was sprayed at a rate of 6 l d⁻¹ cow⁻¹ after scraping with a frequency of 12 times per day. Work by Swierstra et al. (1995) evaluated a slatted floor versus a solid sloping floor with a central gutter with or without a finish in cow barn. The emissions from inclined solid floors were about 50% of the emission of the conventional slatted floors, and floor finishes did not statistically affect the emissions.

A similar study by Braam et al. (1997b) also evaluated a traditional slatted floor and two solid floor systems; one of the latter was sloped (3%) and drained urine in a urine-gutter while the other was not inclined at all. Both the solid floors were either highly scraped (96 times a day) or normally scraped (12 times a day). The non-sloped solid floor scraped normally had the same ammonia emission as the slatted floor, while the sloped solid floor also normally scraped, further reduced ammonia emission by 21% over the other two systems. Increasing scraping to 96 from 12 times/day decreased ammonia emission by only a marginal 5%, which may not economically justify the extra scraping efforts.

All the urine-feces segregation methods evaluated and reviewed in this article reduced ammonia emissions from livestock barns by about 50% compared to the conventional manure handling systems (mixed urine-feces systems). In addition, some limited flushing after feces scraping from the sloped floors further significantly reduce ammonia emissions. In conclusion, the critical factors that need to be considered in the choice of the method for separating urine from feces are the cost of installing the system, maintenance, and ease versus cost of operation.

Table 2 - Summary of ammonia emissions reduction from manure storages using urine-feces segregation

Animal Species	Segregation method	Emissions reduction (%)	References
Swine	Laboratory studies	99	Panetta et al., 2004
Swine	Conveyor belt	47-49	Lachance et al., 2005; Stewart et al., 2004
Cattle	Pre-cast grooves in concrete floor	46	Swierstra et al., 2001
Cattle	V-shaped pit floor with gutter at the V	50-65	Braam et al., 1997a
Cattle	Sloped (3%) solid floor	21	Braam et al., 1997b

Urease inhibitors

The enzyme urease found in the feces rapidly hydrolyzes urea and uric acid into NH₄⁺-N when urine mixes with feces (Beline et al., 1998). However, urease inhibitors can block this urea hydrolysis and reduce ammonia emissions from the manure (Varel, 1997; Varel et al., 1999; Parker et al., 2005).

In laboratory experiments, two urease inhibitors; cyclohexylphosphoric triamide (CHPT) and phenyl phosphorodiamidate (PPDA), successfully controlled urea hydrolysis in typical cattle and swine slurries (Varel, 1997). At dosages of 10 mg/l, both inhibitors stopped the hydrolysis of urea in cattle waste and swine waste for 4 to 11 days. In contrast, hydrolysis of urea in untreated cattle or swine waste (control) was complete within one day. Weekly addition of the inhibitors was the most effective method of preventing urea hydrolysis. Weekly additions of 10, 40, and 100 mg of PPDA per liter of cattle waste (5-6 g urea L⁻¹) prevented 38, 48, and 70% of the urea, respectively, from being hydrolyzed during a period of 28 days. For the swine waste (2.5 g urea L⁻¹), the same PPDA concentrations prevented 72, 92, and 92%, respectively, of the urea from being hydrolyzed during the same study period. The results of these experiments provide technical strategies for significant control of ammonia emissions from livestock facilities while increasing the fertilizer value of these resources by improving the N:P ratio.

Another laboratory study was conducted to evaluate the effect of rate and frequency of urease inhibitor application on ammonia emissions from simulated beef cattle feed-yard manure surfaces (Parker et al., 2005). The urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) was applied at rates of 0, 1, and 2 kg ha⁻¹, at 8, 16, and 32 day frequencies, and with or without simulated rainfall. Synthetic urine was added every two days to the manure surface. This urease inhibitor applied every 8 days was most effective, with the 1 and 2 kg NBPT ha⁻¹ treatments resulting in 49% to 69% reduction in ammonia emission rates, respectively. According to the authors, the 8-day, 1 kg NBPT ha⁻¹ treatments had the most promising benefit/cost ratios, ranging between 0.48 and 0.60. Although the technical and economic potentials of use of NBPT for reducing ammonia emissions in beef cattle feed yard was demonstrated, the authors cautioned that because of possible buildup of urea in the pen surfaces, higher NBPT application rates may be necessary with time. In an earlier study, Varel et al. (1999) reported accumulation of urea, less concentration of ammonia, and more concentrations of total-N in cattle feedlot manure when 20 mg[NBPT]/kg of manure was applied weekly for six weeks compared with control. Panetta et al. (2004) reported contradictory results when NBPT was applied to swine slurry in laboratory studies. In these laboratory studies, additions of single (76 µl/l) and double (152 µl/l) dosages of NBPT increased ammonia emissions by 50 and 140% compared with the control.

Although use of urease inhibitors seems promising in the laboratory studies, no case studies were found in the literature on the use of these additives in the control of ammonia emissions in full-scale concentrated animal feeding operations (CAFOs). The lack of adoption of urease inhibitors may be attributed to the unknown effects of these chemicals on the crops or pastures where the manure is eventually applied as fertilizer.

pH reduction

Ammonia volatilization is directly proportional to the proportion of un-ionized aqueous NH₃-N in the TAN. When temperature is held constant, pH determines the equilibrium between NH₄⁺-N and NH₃-N in aqueous systems. A lower pH leads to a lower proportion of NH₃-N and, therefore, to a lower potential of ammonia volatilization. Acidification of animal manure for mitigation of ammonia loss relies on this basic principle. The greatest increase in ammonia release takes place between a pH of 7 and 10: below pH 7 ammonia volatilization decreases, and at a pH of about 4.5, there is almost no measurable free ammonia (Hartung and Phillips, 1994).

Past studies have clearly demonstrated the efficacy of pH reduction in the mitigation of ammonia volatilization from livestock manure. The results of these studies are summarized in Table 3. Acidification of pig and cattle slurries using H₂SO₄ from a pH of 8 to a pH of 1.6 reduced ammonia emissions progressively and completely stopped ammonia volatilization at a pH of 5 in pig slurries and at a pH of 4 in cattle slurries (Molloy and Tunney, 1983). Jensen (2002) maintained a pH of 5.5 using H₂SO₄ in swine manure in full-scale swine-confinement buildings with a slatted floor and under-the-floor manure pit. These researchers reported reduction of ambient concentrations of the ammonia by about 75 to 90%, while pigs weight increased by 1074 g/day during the study period compared to the pigs in the control buildings.

In a similar study, Stevens et al. (1989) used H₂SO₄ to acidify cow and pig slurries to a pH of 5.5 and 6.0. At these cow and pig slurries pH-conditions, ammonia volatilization were effectively reduced by 95% in the lab and by 82% in the field. Similar studies (Frost et al., 1990) using sulfuric acid to acidify whole cattle slurry to a pH of 5.5 reduced ammonia volatilization by 85%. Al-Kanani et al. (1992) similarly reported ammonia loss reduction of 75% when sulfuric acid was applied to swine manure in laboratory experiments. Somewhat lower ammonia reductions (14-57%) were reported by Pain et al. (1990) when sulfuric acid was used to lower the pH of cattle slurry to about 5.5. Husted et al. (1991) investigated use of another strong acid (hydrochloric acid) on the acidification of stored cattle slurry, and noted that the addition of 240 meq HCl/l resulted in a reduction of the potential ammonia loss by as much as 90% compared to the control. Safley et al. (1983) reported about 50% reduction in ammonia loss using phosphoric acid within 28 days of dairy cattle manure storage. Al-Kanani et al. (1992) reported significantly more (about 90%) ammonia loss reduction using the same phosphoric acid on swine manure. Phosphoric acid, however, adds P concentration in the manure, which is undesirable. Some of the weaker acids like propionic and lactic acids are as effective as the strong acids, and have been observed to reduce ammonia emissions by as much as 90% when pH of the manure is maintained at 4.5 (Parkhurst et al., 1974).

Other researchers have investigated use of other acidifying additives (aluminium potassium sulfate or alum, ferric chloride, sodium hydrogen sulfate, and calcium chloride) for mitigation of ammonia emissions from livestock manure (Li et al., 2006; Armstrong et al., 2003; Shi et al., 2001; Kithome et al., 1999; Al-Kanani et al., 1992; Husted et al., 1991; Witter and Kirchmann, 1989a; Mackenzie and Tomar, 1987; Molloy and Tunney, 1983). Although most of the additives effectively reduce pH, they are generally not as effective in reducing ammonia loss as the strong acids because they cannot maintain stable pH conditions like their counterparts.

Li et al. (2006) reported 89% reduction in ammonia volatilization when alum was applied at the rate of 2 kg[liquid aluminum sulfate]/m²[surface area]. Armstrong et al. (2003) observed that application of liquid alum equivalent of 45, 90, and 135 kg[aluminum sulfate]/93 m² of broiler litter surface was effective at maintaining in-house ammonia concentrations at below 25 ppm for two weeks, three weeks, and three weeks of the grow-out, respectively. Shi et al. (2001) investigated the efficacy of alum on beef cattle manure. Compared to the control, ammonia emissions reduction during 21 days of monitoring were 91.5% at 4500

kg/ha alum and 98.3% at 9000 kg/ha alum. The advantage of alum use in the reduction of ammonia emissions is reduction of soluble phosphorus and the potential for phosphorus runoff or leaching.

The investigations of Witter and Kirchmann (1989a) on the efficacy of calcium and magnesium salts on ammonia loss during aerobic treatment revealed efficiencies of most of these salts ranged between 85-100% efficient within 2-3 weeks and between 23-52% by the seventh week of incubation. Shi et al. (2001) evaluated the efficacy of CaCl₂ on reducing ammonia emissions from beef cattle manure in the laboratory. Compared to the control, ammonia emissions 21 days after application were reduced by 71.2 and 77.5% at 4500 and 900 kg/ha CaCl₂ application. Calcium chloride was less effective than alum at the same application rates. Witter (1991) examined ammonia volatilization after the addition of CaCl₂ to fresh and anaerobically stored manure before land application of the respective slurries. Within 48 h after application, CaCl₂ reduced ammonia loss by 73 in the fresh manure and by 8% in the anaerobically digested manure. Kithome et al. (1999) reported a 10% decrease in ammonia volatilization at the addition of 20% CaCl₂ to poultry manure. This is similar to the maximum 15% ammonia reduction reported by Husted et al. (1991) achieved by addition of 300-400 meq/l of CaCl₂ to cattle slurry. This product is thus only suitable for reducing ammonia in poultry housing, and may not be suitable for reducing ammonia loss from land applied slurries previously stored anaerobically. Al-Kanani et al. (1992) reported a significant reduction in pH and ammonia emission (87%) when monocalcium phosphate monohydrate (MCPM) was applied to cattle manure. Mackenzie and Tomar (1987) also investigated addition of MCPM to liquid hog manure with and without aeration. A decrease in pH was observed with addition MCPM, but the pH increased when addition of the salt addition ceased. During subsequent aeration, total nitrogen (TN) decreased significantly in the control manure, while no significant change was observed in the TN in the manure with MCPM.

Overall, strong acids tested for reducing slurry pH are more cost-effective than the weaker acids and acidifying salts, but are more hazardous for use on the farm than the latter. Therefore, although the acidifying salts and other weaker acids may be less effective than strong acids, they are non-hazardous and relatively low cost; which increases their suitability for on-farm use.

Table 3 - Summary of ammonia emissions reduction from manure storages by lowering pH

Animal Species	Agent or substance	Emissions reduction (%)	References
Cattle and pig	Sulfuric acid	14-100	Molloy and Tunney, 1993; Jensen, 2002; Stevens et al., 1989; Frost et al., 1990; Al-Kanani et al., 1992; Pain et al., 1990
Cattle	Hydrochloric acid	90	Husted et al., 1991;
Cattle and pig	Phosphoric acid	50	Safley et al., 1983
Pig	Phosphoric acid	90	Al-Kanani et al., 1992
Broiler	Alum	89	Li et al., 2006;
Cattle	Alum	91-98	Shi et al., 2001
Cattle	Calcium chloride	71-78	Shi et al., 2001; Witter, 1991
Poultry and cattle	Calcium chloride	10-15	Kithome et al., 1999; Husted et al., 1991;
Cattle	Monocalcium phosphate monohydrate	87	Al-Kanani et al., 1992

Ammonium binding

This category of substances have a high affinity for holding onto NH₄⁺ ions thus reducing ammonia volatilization through decreased concentration of free NH₄⁺ ions. The methods of ammonia binding in some cases are not well understood. A summary of the performance of these substances is provided in Table 4.

Zeolite is a cation-exchange material with a high affinity and selectivity for NH₄⁺ ions due to its crystalline-hydrated properties resulting from its infinite 3-dimensional structure (Mumpton and Fishman, 1977). A layer of 38% zeolite placed on the surface of composting poultry manure reduced NH₃ losses by 44% (Kithome et al., 1999). An earlier study by Witter and Kirchmann (1989b) investigating the efficacy of zeolite on the reduction of ammonia loss from poultry manure during aerobic incubation reported an insignificant 1.5% reduction in ammonia loss when mixed with manure in the ratio of 1:4. Nakaue et al. (1981) observed a reduction of up to 35% ammonia loss by the addition of 5 kg/m² of zeolite to broiler litter. Portejoie et al. (2003) investigated reduction of ammonia loss in pig manure during storage and land application using zeolite, and reported a 71% reduction in ammonia emissions. Li et al. (2006) evaluated the efficacy of zeolite in reducing ammonia emissions from fresh poultry manure in laboratory experiments. Application of typical medium rates of 5% (w/w) zeolite reduced ammonia emission by 81%. Zeolite seems to be more effective for reduction of ammonia in animal slurries and liquid manures than in the solid poultry manures.

Two other additives in this category evaluated for abatement of ammonia emissions in livestock manures are Sphagnum peat moss (*Sphagnum fuscum* peat) and yucca plant extracts (saponins). Al-Kanani et al. (1992) compared the efficacy of several amendments on liquid hog manure and concluded that Sphagnum peat moss was just as effective as the strong acids (reduced ammonia volatilization by as much as 99%), although it did not drop the pH to the same levels as the acids. Barrington and Moreno (1995) observed that a 2-cm cover of floating Sphagnum reduced ammonia loss by as much as 80%. Similar results were reported by other researchers (Al-Kanani et al., 1992), but Witter and Kirchmann (1989b) reported a somewhat lower (24%)

reduction in ammonia emissions when sphagnum peat, mixed in the ratio of 1:4, was used in poultry manure during aerobic incubation. This product also seems to be more effective on the animal slurries than on the solid poultry manure in the same way as zeolite. Kemme et al. (1993) reported ammonia loss reduction of 23% when saponins were applied to pig slurries. Panetta et al. (2004) reports similar results when these extracts were applied to swine slurry in laboratory studies. In this category, saponins do not seem to be as effective in mitigating ammonia emissions as either zeolite or peat moss.

A host of other additives hidden in brand names, presumably to protect commercial interests of their inventors have also been evaluated. Heber et al. (2000) evaluated a commercial manure additive (Alliance[®]) developed by Monsanto EnvironChem (St. Louis, MO.) to improve air quality in swine buildings. Alliance[®] was sprayed into the manure stored in pits underneath slatted floors. Compared to the control, this additive reduced ammonia emissions by 24%, but also further diluted the manure by 20%. The authors estimated the cost of this additive at \$1.38/pig space per year or \$0.50/marketed hog based on 135-day growth cycles, and a product cost of \$3.43/l, and noted that because of the modest reduction in ammonia emission, this additive may not be cost-effective to most producers. Amon et al. (1997) compared the effectiveness of another commercial additive (De-Odorase[®]) to a control (no additive) in broiler production. This product (De-Odorase[®]) significantly reduced ammonia emission by 50% over the control. It is important for producers to ensure effectiveness of the respective additives has been scientifically verified by independent and reputable institutions before they adopt them for use in their facilities.

In summary, amongst ammonia binders, zeolite seems to be more effective for reduction of ammonia emissions from animal slurries and liquid manures than in solid poultry manures. Sphagnum, like zeolite, also seems to be more effective on the animal slurries than on the solid poultry manure. Saponins do not appear to be as effective in mitigating ammonia emissions as either zeolite or peat moss. In general, large quantities of these additives are required, and in most cases (with additives such as the acid/acidic salts); precautions must be taken to safeguard the safety of livestock and farm workers. In addition use of acids may result not only in an undesirable increase in the mineral content of the manure/litter, but also in the corrosion of equipment and structures. It is important to determine appropriate application methods to ensure these additives are most effective.

Table 4 - Summary of ammonia emissions reduction from manure storages using ammonium binders

Animal Species	Binding Agent	Emissions reduction (%)	References
Poultry	Zeolite	1.5-96	Kithome et al., 1999; Witter & Kirchamann, 1989b; Nakau et al., 1981; & Li et al., 2006
Pig	Zeolite	71	Portejoie et al., 2003
Pig	Sphagnum peat moss	80-99	Al-Kanani et al., 1992; & Barrington and Moreno, 1995
Poultry	Sphagnum peat moss	24	Witter & Kirchamann, 1989b
Pig	Saponins (yucca extract)	23	Kemme et al., 1993
Pig	Alliance [®]	24	Heber et al., 2000
Poultry	De-Odorase [®]	50	Amon et al., 1997

Biological treatments

Biological treatments processes are either based on assimilation and immobilization of volatile N or transformation of volatile N into non-volatile inorganic N. The former approaches are geared toward recovering N products from liquid animal waste and include production of: single cell proteins; amino acids; and protein rich aquaculture plants such as duckweed and algae. These alternatives systems will not be reviewed in this article. Transformation of volatile N species to non-volatile species is a major biological treatment process comprising of coupled nitrification and denitrification processes. However, most treatments employ some variation of physical, chemical or components of both physical and chemical unit processes to provide suitable conditions for these processes to occur efficiently and cost-effectively. During nitrification, nitrifying bacteria transforms ammonia to oxidized N (nitrite and nitrate). These compounds are then biologically reduced to environmentally benign N gas (N₂) by denitrifying bacteria. The reaction rate of nitrification is extremely low compared to that of denitrification; consequently, nitrification is the rate-limiting step. Nitrification is the more critical step, and usually receives more attention in biological treatment of wastewaters for removal of ammonia. Common biological treatment systems consist of either single or two bioreactors. The single-reactor-systems are either run alternately in aerobic and anaerobic modes, or have both aerobic and anoxic zones in the same reactor to effect nitrification and denitrification, respectively. In contrast, these processes take place in separate reactors in the two-reactors-systems. To enhance the nitrification kinetics in particular, other features such as cell immobilization on inert materials or other methods of biomass enrichment are incorporated.

Hu et al. (2003) studied a continuous-flow intermittent aeration (IA) process for N removal from anaerobically pre-treated swine wastewater at the laboratory scale. In this study, experiments were conducted at different: influent COD concentrations, aeration:no-aeration ratios, hydraulic retention time (HRT), and solids retention time (SRT). At the HRT of 3 days and SRT of 20 days in the IA tanks, nitrification and denitrification were successfully achieved in the IA process. Nitrogen removal rates surpassed 80%, and nitrite and nitrate were less than 20 mg/l in the effluents. A similar system was evaluated by Zhang et al. (2006) for treating swine manure rich in N. In this study, a bench-scale sequencing batch reactor (SBR) was ran in a cyclic anaerobic-anoxic mode using low-intensity aeration of 1.0 L[air] m⁻³ [wastewater] s⁻¹, coupled with two-step influent feeding. Approximately 97.5% of the TN in the treated manure was removed, with only 15 mg N/l of the oxidized N (NO₃⁺-N) left in the effluent. Luostarinen et al. (2006) evaluated a single-moving bed bioreactor (MBBR) for treatment of anaerobically pre-treated

dairy parlor wastewater and a mixture of kitchen waste and black water. The effect of intermittent aeration and continuous versus sequencing batch operation was also studied. The MBBRs removed 50–60% of N irrespective of the operational mode. Complete nitrification was achieved, but denitrification was impeded by insufficient carbon. The range of N removal in this study was, however, much lower compared with the rates reported by Hu et al. (2003) and Zhang et al. (2006). A likely explanation for these discrepancies may be due to the differences in the influent wastewaters. Loustarinen's studies used milking parlor wastewater, while Hu et al. (2003) and Zhang et al. (2006) systems were run on swine wastewater. Another likely explanation is the confusion in the reporting of N (either as TN, TKN, or TAN).

Pan and Drapcho (2001) reported on a continuous-flow two-reactor (anoxic and aerobic) system for treatment of swine wastewater. The aerobic reactor was maintained at 5mg/l dissolved oxygen. This system was run at HRT of 35 hours in the anoxic and 36 hours in the aerobic, and a recirculation ratio of 1.0. At steady state, ammonia in the effluent was reduced by about 85%, of which 51% was retained as nitrate in the effluent. A similar bench-scale system was evaluated by Ten-Have et al. (1994) for treatment of supernatant from settled sow-manure. This system consisted of separate reactors for nitrification and denitrification and a recycle of mixed liquor from former to the latter. More than 99% of the ammonia was converted to nitrate. Complete denitrification was not accomplished because of inadequate fermentable carbon in the manure supernatant. Molasses was added to provide the extra carbon needed. Shin et al. (2005) investigated a slightly different two-reactor system for biological removal of N from swine wastewater rich in organic matter and N. This system consisted of a submerged membrane bioreactor (MBR) for nitrification followed by an anaerobic upflow bed filter (AUBF) reactor for denitrification. Total N removal efficiency of 60% was achieved at an internal recycle ratio of three times flow-rate. Complete nitrification of the ammoniacal-N was achieved in the process.

Vanotti and Hunt (2000) evaluated an immobilized-cell (encapsulated in polymer resin) system for enhanced nitrification of ammonia in swine wastewater. This system was evaluated for treatment of high-strength swine lagoon wastewaters containing about 230 mg $[\text{NH}_4\text{-N}]/\text{l}$ and 195 mg $[\text{BOD}_5]/\text{l}$. A culture of acclimated lagoon nitrifying sludge immobilized in 3 to 5 mm polyvinyl alcohol polymer pellets was used for this experiment. Alkalinity was maintained with inorganic carbon to ensure a liquid pH within the optimum range (7.7-8.4). In batch treatment, only 14 h were needed for nitrification of $\text{NH}_4^+\text{-N}$. In contrast, it took 10 d for a control (no-pellets) aerated reactor to start nitrification, while as much as 70% ammonia was lost via air stripping. In continuous flow treatment, nitrification efficiencies of 95% were obtained with $\text{NH}_4^+\text{-N}$ loading rates of 418 $\text{mg}[\text{N}]/\text{l}^1$ [reactor] day^{-1} at 12 h HRT. In all cases, the $\text{NH}_4^+\text{-N}$ removed was entirely recovered in oxidized N forms. The immobilized-cell technology thus further enhanced ammonia removal from anaerobic swine lagoons wastewater.

An 8 m^3/day pilot scale two-reactor system was evaluated by Westerman et al. (2000) for treatment of supernatant from settled flushed swine wastewater. The main system consisted of two upflow aerated biofilters connected in series. The aerated biofilters ran at around 27°C, removed about 84% of the TKN, 94% of the TAN, and 61% of the TN. A significant portion of the $\text{NH}_3\text{-N}$ was converted to nitrite plus nitrate nitrogen ($\text{NO}_2+\text{NO}_3\text{-N}$). The TKN, TAN, and TN removal averaged 49%, 52%, and 29%, respectively, when the reactors were ran at around 10°C. The unaccounted N of about 24% could have been lost through ammonia volatilization or through denitrification within the biofilm. Westerman and Bicudo (2002) later evaluated a full-scale nitrification/denitrification system for biological treatment of flushed swine manure in a 3000 finishing-swine facility. The system consisted of a pond with a mixing zone for denitrification (anoxic), and an aeration zone for nitrification, with recirculation from aeration zone to mixing zone, and a recycle from aeration zone to the barns for flushing. Nitrogen reduction in the effluent was 65 to 90%, with more than 90% of the N being in inorganic N form. In addition, significant reduction in odor perception, irritation, and unpleasantness from liquid samples drawn from the treatment system was reported. The report also noted the high energy cost for operation. Another full-scale nitrification-denitrification system is reported by Townsend et al. (2003). This system was constructed to serve 52,800 grow-finish pigs. Nitrification and denitrification occurred in a single wastewater treatment plant centrally located on the farm. Effective TN reduction averaged about 87%. Townsend et al. (2003) also reported significant foam generation during aeration, necessitating continuous use of a defoaming agent for the treatment to continue.

When designed and ran appropriately, these systems can effectively (up to 99%) mitigate ammonia emissions in CAFOs. It appears that the major hindrance is the economics of installing and operating the systems. An important element of biological N removal is the carbon source to complete the denitrification process. Reporting of N (either as TN, TKN or TAN) needs to be well defined to enable inter-comparisons.

3. BUILDING DESIGNS AND MANURE MANAGERMENTS

Accumulated urine and feces on the floor is the main source of ammonia volatilization within the buildings. The longer their residence times on the floor, the more the ammonia volatilization. The manure can be also thinly spread-out, which further exacerbates ammonia volatilization as this provides larger surface areas. Frequent removal of manure may be critical in mitigating ammonia volatilization within the building. Scraping, flushing, slatted floors, conveyor belts or combinations of these systems are currently the most common methods of removing manures from the floors or buildings.

Flushing floors with water achieved a 14 to 70% reduction in ammonia loss compared to use of slatted floors in dairy barns (Voorburg and Kroodsma, 1992; Kroodsma et al., 1993; Ogink and Kroodsma, 1996). Increasing flushing frequency, increasing

the amount of water, and use of fresh water (as opposed to recycled water) further reduce ammonia volatilization within the building (Voorburg and Kroodsma, 1992). However, since these practices may also increase both the volume of the slurry to be handled and the cost of slurry utilization, a compromise between flushing frequency, amount of water, use of fresh water and the respective additional reduction of ammonia losses has to be established.

Kroodsma et al. (1993) investigated the effects of different manure managements on ammonia emissions from freestall dairy houses. Manure scraping did not significantly decrease ammonia emissions, while flushing with water decreased the emissions by up to 70%. Frequent flushing over short periods was more effective than prolonged, but less-frequent flushing. Ogink and Kroodsma (1996) evaluated two cattle manure management systems for reduction of ammonia emissions from cow houses with partially slatted floors. One method was based on scraping the slats and subsequent flushing with water every 2 h, using 20 L[water] d⁻¹ cow⁻¹. The second method was similar, except that 4 g of formalin per liter of flushing water was added. Compared to a control (no scraping or flushing), the former method only lowered the emission by 14%, while adding formalin to the flushing water reduced emissions by 50%. Misselbrook et al. (2006) reported that pressure washing and the use of a urease inhibitor in addition to yard scraping were more effective means of reducing emissions compared with yard scraping alone, while reduction of yard area per animal was also an effective strategy to reduce total emissions.

In slatted floor systems, the frequency of manure removal from the pits under the slats is critical in the management of ammonia emissions within the building (Hartung and Phillips, 1994). Hartung and Phillips (1994) compared four different manure removal strategies: a partially slatted floor (PSF) with a slurry pit emptied every two weeks, a PSF with a sloped slurry channel beneath that is flushed several times a day, a PSF floor with a continuous recirculatory flushing, and a PSF floor with a continuous recirculatory flushing combined with basin and plug. The control was a PSF with slurry pit underneath providing storage for six months. Respective ammonia volatilizations were 20, 60, 40, and 80% less than in the control. In a similar study, Lachance et al. (2005) reported a significant 46% reduction in ammonia emissions when manure was removed every 2-3 days, compared to eight weeks removal frequency in the control. Lim et al. (2004) evaluated several manure management strategies on reduction of ammonia emissions in confined finishing pigs. The strategies included daily flushing, and static pits with 7, 14, and 42 d manure accumulation cycles, with and without pit recharge, with some secondary lagoon effluent after emptying. Flushing and static pit recharge with lagoon effluent resulted in significantly less NH₃. Mean NH₃ emission rates were 15, 27, and 25g d⁻¹ AU⁻¹ for the 1, 7, and 14 d cycles without pit recharge, and 10, 12, and 11 g d⁻¹ AU⁻¹ for the 7, 14, and 42 d cycles with pit recharge, respectively. Mean daily NH₃ emissions from the rooms with static pits were 51 to 62% lower with recharge than without recharge. In summary, less NH₃ emissions occurred when pits were recharged after emptying, and when pits were emptied more frequently.

In poultry buildings (cage) removing manure twice a week using belts, or weekly with drying manure on belts reduced NH₃ emission from battery cage houses by 60% or more compared to allowing manure stay on the belt. However, daily removal has the potential of further reducing NH₃ emissions, since hardly any degradation then takes place inside the house (Cowell and Apsimon, 1998).

Ammonia volatilization within the buildings is also a function of the building ventilation system. Ventilation would increase NH₃ losses because of reduced resistance to NH₃ transfer into the air above the manure. For example, a common practice to reduce elevated NH₃ levels in poultry houses is to increase ventilation rates above the values needed for proper litter moisture control. The increased ventilation rates reduce NH₃ concentration in the house, but translate directly into higher NH₃ emissions as well into costs of running the fans.

4. EMISSIONS CAPTURE AND TREATMENT

Important mitigation strategies of ammonia and other gaseous emissions involve capturing or trapping the fugitive gases and subsequent treatment of the respective captured emissions. These strategies can be put into two broad categories: (i) filtration and biofiltration, and (ii) use of permeable and impermeable covers.

Filtration and biofiltration

Filtration is more of a physical-chemical process while biofiltration not only traps but also biologically degrades or converts trapped compounds into their benign forms. Removing NH₃ from vented air using filters or scrubbers (water and acid) is feasible where barns are mechanically ventilated (Sommer and Hutchings, 1995; Groot Koerkamp, 1994). In most cases, the practical applications of these cleaning devices are limited due to their relatively high cost and technical problems due to dust, especially in poultry and swine houses.

Sun et al. (2000) describes a 20-cm deep biofilter consisting of a mixture of compost and wood chips tested for removal of NH₃ from swine housing ventilation air. On average, this system removed 83% of ammonia in the carrier air at biofilter moisture content of 50% at a retention time of 20s. Tanaka et al. (2003) also reported a reduction of 94% in ammonia from composting air in a biofilter consisting of finished compost (of cattle manure and sawdust) within the first 72h of treatment. Hong and Park (2005) reported 100% ammonia removal efficiency from air from a composting pile (of dairy manure mixed with crop residues) in a 50-cm deep, 50:50 manure compost to coconut peels biofilter. Sheridan et al. (2002) evaluated a pilot scale wood chip biofilter for reducing ammonia from exhaust air from a pig finishing building. A 50 cm deep biofilter made from 20 mm screen size wood

chips efficiently removed between 54 and 93% ammonia depending on volumetric loading rate. A filter bed moisture level of 63% or greater was recommended to maintain the biofilter efficiency. A biofilter consisting of a mixture of pine and perlite removed 95.6% ammonia from ventilation air from a swine facility in a pilot-scale system (Chang et al., 2004). Kastner et al. (2004) reported that a biofilter made of pre-screened yard waste compost reduced ammonia by 25 to 95% in ventilation air from a modern 2400-sow farrow-to-wean unit, depending on residence time and inlet ammonia concentration. Martinec et al. (2001) evaluated several biofilter materials (biochips, coconut peels, bark-wood, pellets+bark, and compost) for reduction of ammonia from swine operations. Ammonia reduction with these materials ranged between 9 and 26%.

There is a broad range of biofilter efficiencies in the removal of ammonia in carrier-air. The wide range of performances (9-100%) reported in the literature may be attributed not only to the wide range of biofilter-materials, but also on other factors such as maintenance of optimum moisture in the filter bed, the residence time of the air in the biofilter (Sun et al., 2000; Hartung et al., 2001; Tanaka et al., 2003), the ammonia load in the incoming air (Sheridan et al., 2002; Kastner et al., 2004), and how well the microbial community is established in the biofilter. Properly designed and ran systems can effectively mitigate ammonia emissions from livestock operations.

For the readers interested in more details on acid scrubbers and trickling filters, a comprehensive review of these technologies for treatment of exhaust air from pig and poultry houses in the Netherlands has recently been completed (Melse and Ogink, 2005). In that review article, ammonia removal in acid scrubbers ranged from 40 to 100%, with an overall average of 96%, while ammonia removal efficiency in biotrickling filters ranged from -8 to +100% with an overall average of 70%. Process control with pH and automatic water discharge were sufficient to guarantee ammonia removal efficiency in acid scrubbers. The review concluded that improvement of process control is required in biotrickling filters to guarantee ammonia removal efficiency. Recent results (Kosch et al., 2005) are similar to values found the review paper.

Impermeable and permeable covers

The simplest control method to mitigate ammonia emissions from storage and treatment systems open to the atmosphere is to use a physical cover to contain the emissions. Impermeable covers, which trap gases released from such systems, are regularly used in conjunction with scrubbers or biofilters. The effectiveness of these covers depends not only on their trapping efficiency, but also on the effectiveness of the scrubber or the biofilter with which they are used in combination. Permeable covers trap and bio-transform ammonia just like biofilters, and include materials such as straw, cornstalks, peat moss, foam, geotextile fabric, and Leca[®] rock. The performances of impermeable and permeable covers are summarized in Table 5.

In comparison to an uncovered control, two impermeable covers; a floating film (two 2-mm thick polyethylene film layers glued together) and a tarpaulin, effectively reduced ammonia emissions from swine manure lagoons by 99.7 and 99.5%, respectively (Funk et al., 2004). Scotford and Williams (2001) reported nearly 100% ammonia reduction from a pig slurry lagoon covered with a floating 0.5-mm thick reinforced ultraviolet light-stabilized opaque polyethylene cover. Funk et al. (2004) reported effective control of ammonia emission using an air-supported 0.35-mm vinyl coated fabric cover installed on an earthen-embanked swine lagoon, but experienced major challenges in controlling the gas leakage. Ammoniacal-N is not soluble in oil; therefore, thin layers of oil (oil-films) can also create impermeable covers over stored manure slurries. Heber et al. (2005) evaluated the efficacy of soybean oil sprinkling on ammonia emission mitigation in tunnel-ventilated swine finishing barns. The oil treated barn resulted in 40% less NH₃ emission than the control barn. Better results have been reported when a layer of vegetable oil was placed on the surface of manure liquid/slurry. Guarino et al. (2006) reported a reduction of ammonia emissions between 79 and 100% when 3 and 9-mm layers of vegetable oil were applied on stored pig and cattle slurries. Portejoie et al. (2003) reported similar ammonia emission reductions (93%) with a 10-mm oil layer. Other laboratory and on-farm studies with a 6 mm rapeseed oil layer indicated control of ammonia emissions by up to 85%, while a thinner 3-mm layer was ineffective (Hornig et al., 1999).

A permeable geotextile cover installed on swine manure storages resulted in 44% reductions in NH₃ emissions, but the cover performance deteriorated after one year (Bicudo et al., 2004). Clanton et al. (2001) reported 37, 72, and 86% reduction in ammonia emissions from swine manure storage with 10, 20, and 30 cm-thick straw covers, respectively, supported on a geotextile fabric. The permeable geotextile fabric itself did not have significant effect on ammonia emissions without a straw layer. Compared to uncovered cattle and pig slurry, surface crust, peat, straw, PVC foil, and Leca[®] rock achieved 24, 32, 60, 26, and 14% maximum ammonia emission reductions, respectively (Sommer et al., 1993). Zahn et al. (2001) reported a 54% reduction of ammonia emissions from a lagoon covered with an acclimated proprietary polymer composite bio-cover. Relative to an uncovered control, Hornig et al. (1999) reported ammonia emissions reduction of 80 to 91% with straw and Pegulit (a natural mineral buoyant material) covers. Development of a surface crust in stored cattle manure was as effective as a 15 cm layer of straw, and reduced ammonia emissions by as much as 20% (Sommer et al., 1993). Guarino et al. (2006) reported effective ammonia reduction from pig and cattle slurry with adequate cover thickness of wheat straw, wood chips, and corn stalks. With 14 cm thick straw, wood chips, and corn stalks covers, ammonia emissions reductions were 100, 91, and 60%, respectively. However, by using 7 cm thick covers, the respective ammonia reductions were only 59, 17, and 37%. In laboratory studies, Xue et al. (1999) reported that 5 to 10 cm straw covers reduced ammonia emissions by 90% from dairy manure storages. Miner and Pan (1995) reported permeable covers configured with straw, zeolite, or a combination of both, effectively reduced ammonia emissions by 90% from manure storages. A permeable polystyrene foam cover was reported to reduce ammonia emissions by 45 to 95% in manure storages

(Miner and Suh, 1997). In other laboratory and field studies, Miner et al. (2003) reported ammonia reductions from swine slurries of about 80% using a 5 cm thick permeable polyethylene foam lagoon cover. Balsari et al. (2006) evaluated a low cost cover (Leca® balls layer) for ammonia emission abatement from swine slurry storage and observed a significant ammonia reduction (up to 87%) with a 10 cm layer of Leca® balls.

Impermeable covers are generally more effective (up to 100%) than permeable covers in ammonia mitigation strategies from manure storages. However, costs for covers vary widely depending on the material used and the method of application. The length of the time the covers will be in place is an important consideration. Removal and clean-up of the material left behind when the useful life of the covers is over is equally important. In addition, if no biofilters are used to clean up the trapped gases under impermeable covers, excessive ammonia and other gaseous emissions may occur during land application. Massey et al. (2003) evaluated the economics of installing impermeable lagoon covers on swine farms, and showed that at \$0.72 to \$3.41/cwt of hog marketed, the initial purchase price of the cover was the biggest hurdle. The second major hurdle is the availability of more land base to receive the conserved N, which could be about 3.5 times larger than open lagoons.

Table 5 - Summary of the performances of permeable and impermeable covers in abating ammonia emissions from livestock manure storages

Cover Type (s)	Emissions reduction (%)	References
Polyethylene	80-100	Funk et al., 2004; Scotford and Williams, 2001; Miner et al., 2003
Tarpaulin	99.5	Funk et al., 2004
Oil films	40-100	Heber et al., 2005; Guarino et al., 2006; Portejoie et al., 2003; Hornig et al., 1999
Geotextile cover	44	Bicudo et al., 2004
Straw covers	37-90	Clanton et al., 2001; Sommer et al., 1993; Horning et al., 1999; Guarino et al., 2006; Xue et al., 1999; Miner & Pan, 1995
Surface crust, peat, & PVC foil	24-32	Sommer et al., 1993;
Leca rock	14-87	Sommer et al., 1993; Balsari et al., 2006
Polymer composite	17-54	Zahn et al., 2001
Pegulit	91	Horning et al., 1999
Wood chips	17-91	Guarino et al., 2006
Corn stalks	37-60	Guarino et al., 2006
Zeolite on permeable cover	90	Miner & Pan, 1995
Polystyrene foam	45-95	Miner and Suh, 1997

5. LAND APPLICATION STRATEGIES

Significant ammonia volatilization can occur when manure is surface-spread to fertilize crop and pasture fields. Minimizing time of manure exposure on the ground surface is the most effective strategy for reducing ammonia emissions during or after field application of manure. Direct injection, prompt plowing-in, increased infiltration, and washing-in after applications are some of the methods available to limit this exposure time. Combining these improved field application techniques with other ammonia holding techniques, such as use of additives, improves the ammonia utilization efficiency of crops and pastures, which further decreases ammonia volatilization. A summary of the efficacy of various application strategies in reducing ammonia emissions is given in Table 6.

In practice, direct injection or immediate incorporation of manure into the soil reduces ammonia losses better than other application methods. Direct injections to within 3-30 cm-depths reduced ammonia volatilization by 47 to 98% compared to surface applications (Hoff et al., 1981; Thompson et al., 1987; van der Molen et al., 1990; Svensson, 1994; Rubaek et al., 1996; Morken and Sakshaug, 1998; Smith et al., 2000; Sommer and Hutchings, 2001). Where direct injection or immediate incorporation has not been an option, other surface placement methods such as band spreading, trailing shoe, and shallow slot injection have been more effective than surface broadcasting. These practices have been reported to reduce ammonia losses by between 39 and 83% compared with surface broadcasting (Thompson et al., 1990a; Svensson, 1994; Frost, 1994; Smith et al., 2000). Some of these researchers (Thompson et al., 1990a; Svensson, 1994), however, have pointed out that, with time, band spreading is not much more effective than surface broadcasting.

Research has also shown ammonia losses from surface applied slurry are inversely related to infiltration. One method of increasing manure infiltration into the soil is manure dilution with water. Manure slurry diluted with water has been observed to reduce ammonia losses by 44 to 91% (Sommer and Olesen, 1991; Stevens et al., 1992; Frost, 1994; Morken and Sakshaug, 1998). Another method of increasing infiltration is cultivating the soil surface or increasing the surface roughness. Cultivating the soil surface before surface application of slurry reduced ammonia losses by between 40 and 90% compared to uncultivated soils (Sommer and Thomsen, 1993). A similar method of increasing infiltration is cultivating the top 6 cm of the soil to mix applied slurry with soil. This manure-soil mixing reduces ammonia loss by as much as 60% compared to surface application (Van der Molen et al., 1990). Other research has shown infiltration is also higher at low soil moisture contents, and slurry application at lower soil moisture reduces ammonia loss by as much as 70% (Sommer and Jacobsen, 1999). The inverse relationship between ammonia loss and the rate (volume/area/time) of slurry application suggests intermittent slurry application might also reduce ammonia loss because of improved infiltration (Thompson et al., 1990b).

Ammonia losses from manure applied during crop growth periods may be reduced by using trail hoses, which apply the slurry onto the soil between rows of plants (Bless et al. 1991; Holtan-Hartwig and Bockman, 1994) or by using a trailing shoe (Smith et al., 2000). The reduced ammonia loss is attributed to immediate absorption of NH₃ by plant leaves and roots, reduced slurry exposed surface, and canopy modified microclimate not favorable for ammonia volatilization (Holtan-Hartwig and Bockman, 1994; Thompson et al., 1990).

Atmospheric conditions play an important role in ammonia loss reduction during slurry application. Sommer et al. (1991) reported a linear increase in ammonia volatilization between 0 and 19°C during a 24 h period. In the same study, ammonia loss increased significantly when wind speed increased to 2.5 m/s, but no consistent increase in ammonia loss was recorded between 2.5 and 4.0 m/s wind speeds. In an earlier study, increasing wind speed from 0.5 to 3.0 m/s increased ammonia loss by about 29% in 5 days (Thompson et al., 1990b). These observations suggest manure applications should be scheduled during non-windy periods. In practice, direct manure injection or manure incorporation into the soil adds to the costs of manure application. However, the cost of injection or manure incorporation into the soil during land application to reduce ammonia emissions may be recaptured in terms of better crop yields due to a more efficient utilization of the applied manure. Considering other environmental benefits accruing from reduced ammonia loss, as well as costs that may be incurred in legal conflicts due to ammonia emissions, these practices can be economically justified.

Table 6 - Summary of livestock manure application strategies for abatement of ammonia emissions

Application Strategy	Emissions reduction (%)	References
Direct injection	47-100	Hoff et al., 1981; Thompson et al. 1987; Rubaek et al., 1996; Morken & Sakshaug, 1998; Smith et al., 2000; Thompson & Meisinger, 2002 ; Svensson, 1994; Van der Molen et al, 1990; Huijsmans et al., 2003; Hansen et al., 2003.
Slot injection	80-92	Morken & Sakshaug, 1998; Frost, 1994; Huijsmans et al., 2001
Band application	0-65	Thompson et al., 1990a; Smith et al., 2000; Morken & Sakshaug, 1998; Huijsmans et al., 2001
Trailing shoe	43	Smith et al., 2000
Slurry dilution	44-91	Morken & Sakshaug, 1998; Frost, 1994; Sommer & Olesen, 1991;
Low soil water content	70	Sommer & Jacobsen, 1999
Soil surface cultivation	40-90	Sommer & Thomsen, 1993; Van der Molen et al, 1990; Huijsmans et al., 2003; Rochette et al., 2001.

SUMMARY AND CONCLUSIONS

Reducing N excretion through dietary changes can effectively mitigate ammonia emissions from livestock operations. In ruminants, reducing the CP intake by as little as 5% can reduce ammonia emissions by as much as 74% from excreted manure. For non-ruminants, similar ammonia emission reductions have been observed by replacing CP with amino acids.

All of the urine-feces segregation methods evaluated and reviewed have reduced ammonia emissions from livestock barns by about 50% compared to the conventional manure handling systems. Therefore, the critical factors that need to be considered in making the choice of method for separating urine from feces from these method are the cost of installing the system, maintenance, and ease versus cost of operation. The closely related use of urease-inhibitors for control of ammonia emissions in CAFO has been somewhat successful at the laboratory level, but there is no pilot or full-scale application reported in the literature. The lack of information of its efficacy at pilot or full-scale facilities may partly explain why urease-inhibitors have not been employed for on-farm control of ammonia emissions. This lack of adoption may also be attributed to the unknown effects of these chemicals on the crops or pastures where the treated manures are ultimately utilized.

Acids and acidifying salts are effective at holding ammonia in ammonium form. However, strong acids reduce slurry pH more cost-effectively than the weaker acids and acidifying salts. In addition, because strong acids are more hazardous for use on the farm than acidifying salts and weaker acids, the latter although less effective than the strong acids, they are more suitable use on-farm. Among ammonia binding amendments, zeolite and sphagnum are more effective for reduction of ammonia loss in manure slurries or liquid than in solid poultry manures. Yucca extract (saponins) does not seem to as effective as either zeolite or peat moss in mitigating ammonia emissions.

There are a number of other amendments with various brand names, but their mode of operations is not known. It is important for producers to ensure that the effectiveness of these additives have been scientifically verified by independent and reputable institutions before they can adopt them for use in their facilities. Often, large amounts of the product are required and in most cases such as the use of acid/acidic salts, precautions must be taken to safeguard the safety of livestock and farm workers. In addition use of acids may result not only in an undesirable increase in the mineral content of the manure/litter, but also in the corrosion of equipment and structures. Selection of appropriate application methods for effective use of these additives is very important. Currently, there is a lack of standardized application and evaluation protocols for these additives. Impermeable covers are more effective than permeable covers in ammonia mitigation strategies from manure storages. However, if no biofilters are used to clean up the trapped gases under impermeable covers, excessive ammonia and other gaseous emissions

may occur during land application. Although the biggest hurdle in the installation of impermeable lagoon covers on swine farms is the initial purchase price of the cover, another major consideration is availability of more land base required to receive the conserved N.

Biofilters exhibit a wide range of performances (9 to 100% effectiveness) in the removal of ammonia in carrier-air. This variability in effectiveness may be attributed not only to the wide range of biofilter-materials, but also on other factors such as maintenance of optimum moisture in the filter bed, the residence time of the air in the biofilter, the ammonia load in the incoming air, and how well the microbial community is established in the biofilter. However, these systems can effectively be used to mitigate ammonia emissions from livestock operations. There is also a wide variation in the effectiveness of other ammonia filters (scrubbers and trickling filters). Process control with pH and automatic water discharge were sufficient to guarantee ammonia removal efficiency in acid scrubbers, while process control is required in biotrickling filters to guarantee ammonia removal efficiency.

Although more costly, direct manure injection or manure incorporation into the soil are the most effective (up to 98%) methods for mitigating ammonia emissions amongst methods of manure application to soil. However, the extra costs of injection or incorporating manure into the soil may be recaptured in terms of better crop yields because of more efficient utilization of the applied manure. Direct injection, or immediate incorporation into the soil become not only attractive practices, but also may be economically viable considering other environmental benefits accruing from reduced ammonia volatilization, as well as cost that may be incurred in legal tussles due to the ammonia releases.

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