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Effect of Adding Alum or Zeolite to Dairy Slurry on Ammonia Volatilization and Chemical Composition

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ABSTRACT

Development of cost-effective amendments for treating dairy slurry has become a critical problem as the number of cows on farms continues to grow and the acreage available for manure spreading continues to shrink. To determine effectiveness and optimal rates of addition of either alum or zeolite to dairy slurry, we measured ammonia emissions and resulting chemical changes in the slurry in response to the addition of amendments at 0.4, 1.0, 2.5, and 6.25% by weight. Ammonia volatilization over 96 h was measured with six small wind tunnels with gas scrubbing bottles at the inlets and outlets. Manure samples from the start and end of trials were analyzed for total nitrogen and phosphorus, and were extracted with 0.01 *M* $CaCl_2$, 1.0 *M* KCl, and water with the extracts analyzed for ammonium nitrogen, phosphorous, aluminum, and pH. The addition of 6.25% zeolite or 2.5% alum to dairy slurry reduced ammonia emissions by nearly 50 and 60%, respectively. Alum treatment retained ammonia by reducing the slurry pH to 5 or less. In contrast, zeolite, being a cation exchange medium, adsorbed ammonium and reduced dissolved ammonia gas. In addition, alum essentially eliminated soluble phosphorous. Zeolite also reduced soluble phosphorous by over half, but the mechanism for this reduction is unclear. Alum must be carefully added to slurry to avoid effervescence and excess additions, which can increase soluble aluminum in the slurry. The use of alum or zeolites as on-farm amendment to dairy slurry offers the potential for reducing ammonia emissions and soluble phosphorus in dairy slurry.
(**Key words:** amendments, ammonia volatilization, dairy manure, phosphorus)

Abbreviation key: TKN = total Kjeldahl nitrogen, **TKP** = total Kjeldahl phosphorous.

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INTRODUCTION

Development of cost-effective treatments for animal manure has become a critical problem as the number of animals raised on farms continues to grow and the land mass available for manure spreading continues to shrink. The three main nutrient issues for on-farm treatment of manure are: nitrogen (N) loss through ammonia volatilization, excess phosphorus (P), and the balance of N to P (N/P ratio). This study addresses the potential for using a chemical additive, alum or zeolite, to reduce ammonia volatilization and P availability from dairy slurry.

Up to 50% of the N in freshly excreted manure can be lost with the conversion of urea, which is a primary component of urine, to ammonia and the subsequent volatilization of the ammonia to the atmosphere (Bussink and Oenema, 1998; den Boerb et al., 1990; Muck and Richards, 1983; Phillips et al., 1999). This ammonia loss impacts both agricultural and nonagricultural ecosystems in terms of a direct loss of plant available N to the farmer, a reduced N/P ratio which accelerates P build-up in soils, and eutrophication in aquatic and low-N input ecosystems through atmospheric transport and deposition (ApSimon et al., 1987; Asman, et al. 1994, 1998; van Breemen et al., 1982). Volatilized ammonia also reacts with sulfur compounds released from combustion of carbon fuels to form the majority of the 2.5-μ size particulates. These particulates are of particular concern for human health and are the subject of pending regulation (Confined Livestock Air Quality Committee, 2000).

Phosphorus is a concern because manure is typically spread on agricultural fields at rates in excess of that needed to support crop growth, which has resulted in the accumulation of excess soil P. Manures spread on fields commonly contain N/P ratios of 3/1 to 5/1, while crops require N/P ratios of about 8/1 (Beegle, 1999; Sharpley, et al., 1998). Thus, using manures to meet crop N requirements will simultaneously add excess P to soils and cause soil-test P levels to rise. High soil-test P levels have been found to contribute P to fresh water resources through direct erosion of high P sedi-

ment and surface runoff of P from high soil-test P areas (Sharpley et al., 1998; Sims, 1993; Snyder et al., 1993). Two major factors contributing to the low N/P ratio in manure are the loss of excreted N through ammonia volatilization and the presence of excess P in the diets of farm animals.

One common strategy for treating manure is the addition of amendments such as acidifying agents (alum, iron salts, mineral acids), sequestering agents (zeolites, flocculents), or agents that bind P (alum, calcium salts). However, for an amendment to be commercially viable, it must be reasonably priced, and the benefits must outweigh any potential adverse environmental effects. Two amendments that potentially meet these criteria are alum and zeolite. Alum is commonly used to remove P during sewage treatment; hence, it is widely available at reasonable cost. It is currently used as a litter amendment in the poultry industry, primarily to chemically sequester P (Maurice et al., 1998; Moore and Miller, 1994). However, it can also lower ammonia emissions from poultry houses (Moore, 1998). Alum has also been used as an amendment in feedlots (Dao, 1999), during composting of poultry manure (Kithome et al., 1999), and to reduce P content in dairy wastewater (Jones and Brown, 2000). Zeolite is a silicate clay mineral widely available in the western United States and Mexico. Zeolite is a cation-exchange medium that has been used to reduce ammonia in water (Kithome et al., 1998) and in products such as kitty litter to reduce ammonia emissions from urine. Zeolite has been used as an amendment to poultry litter (Maurice et al., 1998), in anaerobic reactors treating cattle manure (Borja et al., 1996), during composting of poultry manure (Kithome et al., 1999), and as a filtration agent in deep-bedded cattle housing (Milan et al., 1999). The primary cost component for zeolite is the cost of shipping. The efficacy of alum or zeolite as an amendment to dairy slurry has not been tested.

The general objective of this research was to evaluate the potential benefits and suitability of alum and zeolite as on-farm manure treatment amendments for dairy slurry. Specific objectives were: 1) to determine the optimum concentrations of alum and zeolite for reducing ammonia losses from dairy slurry, 2) to quantify the effectiveness of these amendments on ammonia volatilization, 3) to assess the effects of these amendments on slurry properties such as pH, soluble P, exchangeable ammonium-N, and water soluble Al, and 4) to elucidate the chemical basis for treatment effects.

MATERIALS AND METHODS

Manure Collection and Treatment

Slurry was collected from the holding pit at the base of the free-stall dairy barn at the Beltsville Agricultural Research Center after 1 h of agitation. Cows in the barn were fed a TMR and manure was collected using a continuously running mechanical scraper that scraped the manure up to 100 m before depositing it in the holding pit. Bedding consisted of a small amount of sawdust, and the DM content of the slurry ranged from 9 to 11%.

Table 1. Chemical composition of zeolite.[1]

Chemical	Percent
SiO_2	65.35
Al_2O_3	12.72
Na_2O	2.60
K_2O	3.62
CaO	2.14
MgO	0.59
Fe_2O_3	1.51
TiO_2	0.05
P_2O_5	0.02
MnO	0.02

[1]Zeolite from Nicole Mountain, color white, 200 mesh, ammonium exchange capacity 1.84 to 1.96 meg/gm, and principal mineral clinoptilolite. Provided by Southwest Mining Group, Inc., Laguna Hills, CA.

On four separate dates, a bulk sample of about 24 L of slurry was collected and subdivided into appropriate lots for use as untreated controls, or for treatment with alum or zeolite. Six wind tunnels were available for studying ammonia volatilization for each trial. For trial one, the treatments consisted of 0.4, 1.0, 2.5, and 6.25% alum (commercial grade, granular aluminum sulfate, 48.5% $Al_2(SO_4)_3 \cdot 14H_2O$) along with two controls with no additives. Additions were calculated on a weight basis. For trial two, zeolite (Table 1) was used at the same rates instead of alum. For trial 3, 2.5 and 6.25% alum and zeolite were used along with two controls. In trial four, replicates of 2.5% alum and zeolite were used along with two controls. The first two trials identified optimum levels of alum and zeolite based on their ammonia loss characteristics, while the last two trials provided a direct comparison of alum versus zeolite on ammonia loss. After adding the appropriate amendment at the desired rate, the slurry was mixed with a large dough mixer. Each slurry treatment was then subdivided into four 1-L containers and three metal pans for DM determination. Two of the containers were placed on ice and transported to the wind tunnel site within 2 h of collection and treatment, the third was put in refrigerator (4°C) for short-term storage before analysis, and the last container was stored at −20°C.

Ammonia Volatilization

Ammonia volatilization was assessed with a system of small mobile wind tunnels described in detail by

Meisinger et al. (2001). Briefly, each tunnel consists of two components, an inverted U-shaped polycarbonate canopy (2.0 × 0.5 m), and an attached metal plenum, which housed a variable speed fan, a six-spoked air sampler, and an anemometer to continuously monitor wind speed. Gas scrubbing bottles with dilute (0.002 mol L^{-1} H_3PO_4) phosphoric acid and small vacuum pumps were used to trap ammonia from the air stream entering each canopy and the air stream exiting the slurry-treated area. The wind tunnels were housed in a heated building equipped with an intermittent exhaust fan, which operated at a rate to remove about four building air volumes per hour. An exhaust plenum made of plastic sheeting was used to channel exhaust air from the wind tunnels to the building exhaust, thus reducing recirculation of ammonia-enriched air from the wind tunnels. Temperatures in the building ranged from 9 to 14°C over 24 h. A constant wind-tunnel air velocity of 0.5 m/s was used for all trials. Air flow was measured with a calibrated thermoanemometer, see Meisinger et al. (2001) for details. Controlled loss and recovery studies with ammonium solutions under these same conditions have reported ammonia recoveries of 104 ± 6%, see Meisinger et al. (2001) for details.

Upon arrival at the wind tunnel site, the pH of the contents of each container was determined with a combination glass-calomel electrode, which was inserted directly into samples and allowed to stabilize for about 3 min. The combined 2-L quantity of each treatment was then spread on a fiberglass tray (46 × 66 cm) and placed in the wind-tunnel canopy. Each tray was weighed before and after adding the slurry. Ammonia emissions were monitored continually in each trial for 96 h using 11 sampling intervals. Sampling intervals ranged from 1.5 h at the onset of trials to 16 h (overnight) toward the end of each trial (Figure 1). At each sampling time, the exposed gas scrubber bottles were changed and exposed bottles were immediately brought to appropriate volumetric levels and mixed, and subsamples were stored at 4°C in glass bottles for future analysis. Acid samples were analyzed for ammonium nitrogen (NH_4^+-N) using a Technicon Autoanalyzer and the indophenol blue method according to EPA method 350.1 (EPA-600/4-79-020). At the end of each trial, each tray was weighed, and the manure was transferred to 1-L polyethylene containers, where it was mixed using a spatula. A subsample was then taken to determine DM, with the remainder divided into two portions, one portion for short-term storage at 4°C and the second for long-term storage at −20°C.

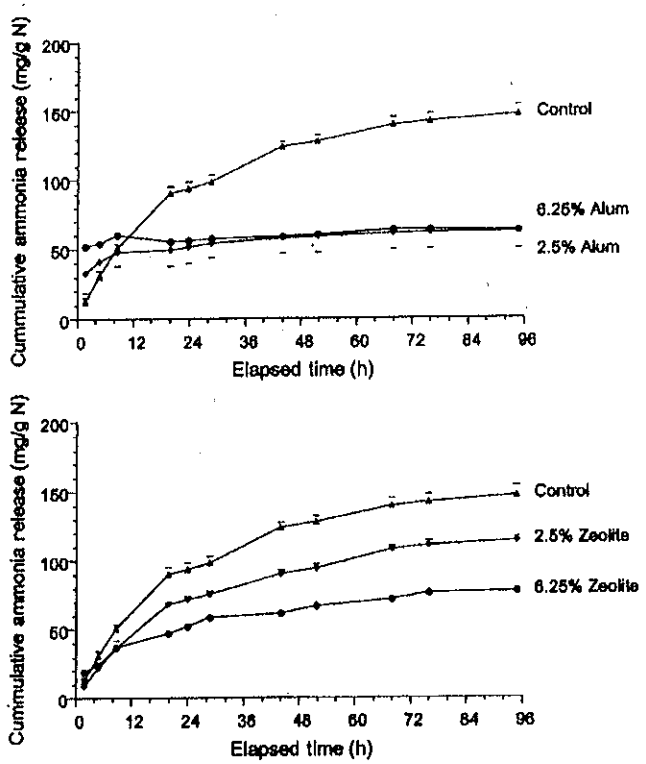

Figure 1. Cumulative ammonia release over 96 h. The top graph shows release following treatment of slurry with 2.5% alum (diamonds, n = 3) and 6.25% alum (circles, n = 1) along with results for untreated controls (triangles, n = 4). The bottom graph shows release following treatment with 2.5% zeolite (diamonds, n = 3) and 6.25% zeolite (circles, n = 1) along with the same controls shown in the top graph. Ammonia release data were normalized by dividing measured values by individual, initial, total Kjehldahl nitrogen values. Data are raw means and standard errors of the means for trials three and four.

Chemical Analyses

Chemical analyses were conducted on the manure and several extracts of the manure to document the effects of the various treatments. After short-term storage at 4°C, undried manure samples from the untreated and amended slurries at the start and the end of the trials were digested for total N (**TKN**) and total P (**TKP**) by the Kjeldahl method using a block digester. The diluted digest was analyzed for ammonium N and ortho-phosphate P with a Technicon Autoanalyzer according to the Technicon industrial method no. 334-74W/B. Total N and P results were expressed on a wet weight basis. The slurry moisture content was determined by drying separate samples to a constant weight in a 100°C forced-air draft oven.

Thawed manure samples were extracted with three solutions: 0.01 *M* $CaCl_2$, 1 *M* KCl, and double-distilled water to document the effects of the amendments on the solution chemistry of the slurry. Approximately 1 g of manure was weighed out and dissolved in 10 ml of extracting solution in a polyethylene test tube. The tube

was capped, vortex mixed, shaken for 2 h, and then centrifuged at 1000 × *g* for 20 min. The pH of the supernatant was measured with a combination glass electrode, and then the supernatant was filtered through a 0.5 μ filter, acidified to pH < 2.0 with hydrochloric acid, and refrigerated. Stored samples were analyzed for ammonium-N and ortho-phosphate using a Technicon autoanalyzer as described above. The aluminum content of the extracts was determined with an atomic absorption spectrophotometer (Bertsch and Bloom, 1996).

Calculation and Statistical Analyses

A significant challenge in this study was determining how to best normalize results to allow comparisons across different trials and treatments. For pH, normalization was not necessary because of similar pH among trials and because pH measures H^+ activity on a logarithmic scale. However, the ammonia volatilization values and NH_4-N and P results from the various extractions required normalization to be interpretable. The most common normalization method is to express results as a percentage of the slurry DM. However, slurry composition varied from trial to trial and the alum and zeolite additives significantly altered the DM content in a nonuniform manner. Therefore, these data were normalized by dividing by TKN or TKP values at the start and end of trials as appropriate. For example, ammonia volatilization data and NH_4-N extraction data at the start of trials are expressed as the ratio of measured N to the corresponding initial manure TKN (which was 2.7 to 3.4 mg of N/g of slurry), while P data are expressed as the ratio of P extraction data at the start of trials to the corresponding initial manure TKP (0.4 to 0.5 mg of P/g of slurry). No normalization factor was used for the Al data because slurry Al levels were consistently low and any change in Al was substantial and due to an added amendment. The Al data are expressed as milligrams of Al per gram of wet slurry.

The experimental design was analyzed as a completely randomized design, with the treatments from each trial being pooled together for analysis. The wind-tunnel data were summarized by simple ammonia emission versus time plots with each treatment's standard error of the mean listed on the plots. The extraction data were analyzed using PROC GLM in SAS version 8 (SAS Institute, 1999). The model included the factors: TREAT (treatment, e.g., 2.5% zeolite), CATEGORY (alum, zeolite, or control), SOLUT (extracting solution, including manure if appropriate), and a TREAT*CATEGORY*SOLUT. Means and standard errors were obtained using the LSMEANS option because of unequal number of replicates for each treatment.

RESULTS AND DISCUSSION

Ammonia Volatilization

Cumulative ammonia release over 96 h for trials 3 and 4 are shown in Figure 1a and b. Ammonia emissions occurred very rapidly in the unamended control slurry, with about 65% of the total loss occurring within 24 h of exposure in the wind tunnels. Beyond the first 24 h, the control slurry lost ammonia at a nearly linear rate of about 1.5% of the slurry total N per day. The total ammonia loss from the control slurry while in the wind tunnels was about 15% of the initial slurry TKN; of course, additional ammonia loss had already occurred in the free-stall barn.

Ammonia losses with either 2.5 or 6.25% alum were negligible beyond the first 12 h. Compared with controls, total cumulative ammonia losses were reduced 58 ± 6% and 57 ± 10% for 2.5 and 6.25%, respectively. The initial losses in the 0 to 12 h time frame are probably due to degassing of previously dissolved ammonia in solution, and are likely attributed to the fact that the alum did not instantly react with the slurry, but took several hours to complete the reaction at the relatively cool temperatures (12 to 14°C) at the onset of the trials. The mode of action for the alum was a simple acidification of the slurry (Table 2), which is an effective way to conserve ammonia because the percentage of total solution ammoniacal N (NH_4-N plus NH_3-N) that is dissolved as NH_3 gas is about 39, 6, 0.6, 0.06, and 0.006% at pH values of 9, 8, 7, 6, and 5; respectively (Court et al., 1964). Alum additions of 2.5 and 6.25% reduced slurry pH below 5 (Table 2) but did not affect water extractable NH_4-N at the start of the studies (Table 3). Water and KCl extractable NH_4-N at the end of the studies (Table 3) were increased with the higher rates of alum because the reduced ammonia volatilization conserved NH_4^+-N in the acidified slurry. Alum additions of 0.4 and 1.0% did not reduce slurry pH below 6.5 (Table 2), which resulted in minimal ammonia conservation. These results support the work of Bussink et al. (1994), who show that the addition of nitric acid to slurries to lower the pH below 5 can virtually halt ammonia emissions. Stevens et al. (1992) also reported reduced ammonia emissions from surface application of acidified cattle slurry. In this study, treating dairy slurry with alum was shown to be a successful technique for acidifying the slurry with a concomitant reduction in ammonia volatilization. The alum amendment also affected P and Al in solution, which is discussed below.

Zeolite additions at 2.5 and 6.25% also reduced ammonia emissions compared to controls, by 22 ± 6% and 47 ± 10%, respectively. The zeolite reacted more slowly with the slurry than did the alum; lowering both the

Table 2. The pH of raw manure and solutions of manure dissolved in calcium chloride, potassium chloride, or water. Measurements were made for manure sampled at the start and the end of individual trials.

	pH at start								pH at end					
	$CaCl_2$		KCl		Water		Manure		$CaCl_2$		KCl		Water	
Treatment	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
0.4% Alum	6.8	0.2	7.4	0.2	7.2	0.2	7.0	0.3	7.3	0.1	7.5	0.1	7.3	0.1
1% Alum	6.4	0.2	7.0	0.2	7.2	0.2	5.9	0.3	7.0	0.1	6.6	0.1	6.9	0.1
2.5% Alum	4.7	0.1	4.7	0.1	4.7	0.1	5.1	0.1	4.8	0.1	4.8	0.1	4.8	0.1
6.25% Alum	4.0	0.1	4.0	0.1	4.0	0.1	4.0	0.1	4.1	0.1	3.9	0.1	3.9	0.1
Control	7.1	0.1	8.1	0.1	7.7	0.1	7.3	0.1	7.8	0.0	8.2	0.0	7.9	0.0
0.4% Zeolite	7.1	0.2	8.1	0.2	7.6	0.2	7.4	0.3	8.4	0.1	8.5	0.1	8.4	0.1
1% Zeolite	7.1	0.2	8.2	0.2	7.6	0.2	7.3	0.3	8.4	0.1	8.6	0.1	8.4	0.1
2.5% Zeolite	6.7	0.1	8.0	0.1	7.8	0.1	7.1	0.1	8.3	0.1	8.5	0.1	8.2	0.1
6.25% Zeolite	7.0	0.1	7.9	0.1	7.8	0.1	7.4	0.2	8.4	0.1	8.6	0.1	8.5	0.1

initial rapid rate of loss during the 0- to 24-h period and the linear rate of loss beyond 24 h (Figure 1b). The reduced emissions were not the result of acidification because the pH of zeolite-treated slurries were consistently above 7 (Table 2). The mode of action is most likely a reduction of the slurry dissolved NH_4^+-N due to an equilibrium between dissolved total ammoniacal-N and exchangeable NH_4^+-N, which is held on organic and inorganic exchange sites in the slurry. The addition of zeolite increases the number of NH_4^+-N exchange sites, decreasing the quantity of dissolved ammoniacal-N, and thus the quantity of equilibrated NH_3-N gas available for ammonia volatilization. Evidence for this mode of operation for zeolite is shown by the lack of change in water pH for all levels of zeolite at the start of the study (Table 2) and the decrease in water extractable NH_4^+-N with increasing rates of zeolite at the start of the studies (Table 4). At the end of trials, the water extractable NH_4^+-N was lower for all zeolite treatments compared with the control (Table 4), while the KCl extractable NH_4^+-N increased as the rate of zeolite amendment increased (Table 4). This increase in KCl extractable NH_4^+-N is due to the exchange of K^+ in the KCl extract with the NH_4^+-N on the zeolite exchange complex. Potassium is widely used in soil analysis to replace adsorbed NH_4^+-N on clays and thereby measure both dissolved and adsorbed NH_4^+-N in a KCl extract (Mulvaney, 1996). Kithome et al. (1998) present detailed data on the adsorption and desorption of NH_4-N by zeolite, which shows that the speed of absorption is affected by the solution NH_4-N concentration and the pH; they conclude that zeolite has excellent ammonium-N adsorbent properties. Additions of 0.4 and 1.0% zeolite did not substantially reduce water extractable, or KCl extractable, NH_4^+-N (Table 4), which resulted in minimal ammonia volatilization reductions. Because zeolite reduces ammonia losses by acting as a sink for soluble NH_4^+-N, their effectiveness will increase as the rate of addition increases. The optimum rate of zeolite will also vary with the quantity NH_4^+-N in a specific slurry. Treating dairy slurry with zeolites was not as effective as alum in controlling ammonia volatilization (compare Figure 1a with 1b), but zeolite did successfully sequester NH_4^+-N with a concomitant reduction in am-

Table 3. The percentage of soluble ammonia relative to total Kjehldahl nitrogen for solutions of manure dissolved in calcium chloride, potassium chloride, or water. Measurements were made for manure sampled at the start and the end of individual trials.

	Extractable ammonia at start (%)						Extractable ammonia at end (%)					
	$CaCl_2$		KCl		Water		$CaCl_2$		KCl		Water	
Treatment	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
0.4% Alum	50.0	2.3	48.9	2.3	45.2	2.3	24.3	4.2	21.5	4.2	23.3	4.2
1% Alum	51.1	2.3	50.7	2.3	46.1	2.3	40.5	4.2	40.0	4.2	38.6	4.2
2.5% Alum	49.0	1.2	51.3	1.2	46.9	1.2	53.2	2.1	52.4	2.1	48.5	2.1
6.25% Alum	49.8	1.6	54.5	1.6	48.0	1.6	47.2	3.0	50.2	3.0	46.9	3.0
Control	48.6	0.8	52.1	0.8	46.6	0.8	18.1	1.5	16.4	1.5	17.7	1.5
0.4% Zeolite	47.1	2.3	52.6	2.3	46.7	2.3	11.5	4.2	10.4	4.2	11.7	4.2
1% Zeolite	39.1	2.3	48.6	2.3	43.2	2.3	7.5	4.2	7.5	4.2	7.6	4.2
2.5% Zeolite	41.5	1.2	53.8	1.2	40.4	1.2	14.2	2.1	15.1	2.1	13.1	2.1
6.25% Zeolite	30.9	1.6	54.5	1.6	31.1	1.6	10.3	3.0	20.2	3.0	10.1	3.0

Table 4. The percentage of soluble P relative to total Kjehldahl phosphorus for solutions of manure dissolved in calcium chloride, potassium chloride, or water. Measurements were made for manure sampled at the start and the end of individual trials.

	Extractable P at start (%)						Extractable P at end (%)					
	$CaCl_2$		KCl		Water		$CaCl_2$		KCl		Water	
Treatment	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
0.4% Alum	5.4	2.7	14.1	2.7	8.0	2.7	6.5	5.6	16.6	5.6	13.8	5.6
1% Alum	0.7	2.7	2.5	2.7	0.2	2.7	1.4	5.6	2.6	5.6	2.0	5.6
2.5% Alum	0.0	1.4	1.5	1.4	0.1	1.4	0.5	2.8	1.1	2.8	1.2	2.8
6.25% Alum	0.1	1.8	1.7	1.8	0.8	1.8	1.0	3.4	1.2	3.4	1.2	3.4
Control	23.5	1.0	66.5	1.0	39.6	1.0	11.1	2.0	39.5	2.0	34.6	2.0
0.4% Zeolite	20.5	2.7	69.6	2.7	48.8	2.7	4.6	5.6	23.7	5.6	18.6	5.6
1% Zeolite	22.2	2.7	67.9	2.7	46.5	2.7	5.1	5.6	28.7	5.6	21.6	5.6
2.5% Zeolite	23.0	1.4	78.5	1.4	42.5	1.4	4.8	2.8	19.6	2.8	18.2	2.8
6.25%	21.7	1.9	80.4	1.9	48.2	1.9	5.6	4.0	12.2	4.0	13.5	4.0

monia volatilization. The effects of the zeolite amendment on soluble P and Al are discussed in the next section.

Phosphorus and Aluminum

The alum and zeolite amendments also had effects on P and Al, which are two other elements of concern in waste management. The effect of alum and zeolite on extractable P are summarized in Table 3. Alum was very effective in reducing soluble P in all three extracts, even at the 0.4% rate of addition where it reduced soluble P about 75% compared to the control. This is consistent with other research by Moore and Miller (1994) and Hsu (1976). Alum reacts with water to form Al hydroxide and sulfuric acid. The soluble Al in an acid environment reacts with soluble P to form relatively insoluble Al-phosphate intermediates that form the reaction sequence from water soluble P to the insoluble variscite-like compounds (Sample et al., 1980).

The 50% reductions in soluble P from the zeolite addition between the start and the end of the studies was unexpected (Table 3). We hypothesize that this could be due to P adsorption on the zeolite mineral and/or to the formation of Ca- or Mg-phosphate mineral intermediates such as octacalcium phosphate or struvite. Alumino-silixate minerals have been shown to retain P through both adsorption and precipitation mechanisms (Sample et al., 1980). The use of the $CaCl_2$ extractant resulted in lower soluble P levels than the other extracts, which indirectly supports the view that a low solubility Ca-phosphate was involved in these soluble P reductions. Which of these two possibilities accounts for the lower P will require further study of the soluble Ca^{++} and Mg^{++} dynamics, as well as P desorption studies. This is an area for future research.

Significant ($P < 0.01$) increases in soluble aluminum were seen, but only for alum treatments of 2.5% or 6.25% (Table 5). The largest effect of alum on soluble Al was at the 6.25% level. The apparent increases in soluble Al between the start and the end of the trials are probably due to the increase in dry matter of the slurries during exposure in the wind tunnels (Al data were not adjusted for slurry dry matter content). Excessive levels of soluble Al in slurries could add a soil acidity management element to farm nutrient management plans. But the specifics of this potential acidity aspect will depend on the farm soil chemical properties, the crop rotation, and liming programs of each individual farm. In any event, it would be best to utilize only enough alum to control ammonia losses (2.5% in this study) and avoid excess additions, which could lead to elevated levels of soluble Al. The zeolite amendment did not increase soluble Al, despite the fact that Al was 12% of the zeolite mineral (Table 1) because the zeolite Al is part of a alumina-silicate clay mineral structure which is insoluble in aqueous extracts.

Physical Effects and Other Observations

Another significant factor for on-farm use of amendments is their physical effects on the slurry. The addition of alum caused an immediate frothing and effervescence of the slurry. This effervescence caused handling difficulties and was thought to have possibly driven off dissolved ammonia through gas stripping. To test this hypothesis, alum was added to slurry in sealed flasks maintained at a constant temperature in a water bath while purified air was passed through the flasks. Any ammonia in the exiting air was trapped in dilute acid in gas scrubbing bottles. The results showed little or no ammonia loss from the slurry. Thus, the effervescence caused by alum appears to mainly affect the physical handling properties of the slurry. On a practical basis, it would be wise to slowly add alum in solution to a slurry pit being agitated until the pH dropped to around

5. This procedure would reduce effervescence and would assure that excess alum was not added. Alum is also a flocculent, and in sewage treatment it is commonly added prior to solid separation in order to increase the efficiency of particulate removal. In this study, the dry matter content of the 2.5% alum treated slurry was slightly greater than controls at the start of trials, but it rose to around 45% at the end of the wind-tunnel trials compared to 20% for the controls. Apparently, alum contributed to greater water loss during the wind-tunnel studies. No physical handling problems or items of note were encountered with the zeolite treatments.

The alum used in this study was a commercial dry (hydrated) product. However, alum is also available commercially in a liquid form. On an equivalent weight basis, the liquid alum is cheaper ($155 per equivalent dry ton; DeltaChemical Corporation, Baltimore, MD) and more acidic (pH 2). This reduced acidity should require the addition of less alum to lower the pH of a manure slurry to five. As a rough estimate, the cost of treating manure should be less than fifty cents per day per lactating cow. Estimating the cost of zeolite treatment is difficult as there is no existing large volume infrastructure for zeolite distribution equivalent to the infrastructure for distributing alum for waste treatment.

Both alum and zeolites have been used on farms for waste treatment. Alum has been used as an in-house treatment for poultry manure (Moore, 1998; Moore and Miller, 1994), on cattle feedlots (Dao, 1999), and to treat dairy wastewater (Jones and Brown, 2000). Zeolite has been used as an amendment in poultry houses (Koelliker et al., 1980) and thermophilic anaerobic digestion of cattle slurry (Borja et al. 1996). The plant availability of the sequestered ammonium in this study was not examined, but several investigators have found the zeolite bound ammonium to be a good slow-release N source for plants (Bartz and Jones, 1983; Lewis et al., 1984; Pirela et al., 1984). In addition, there are many forms of zeolite with different chemical compositions and physical characteristics. These other forms of zeolite may have improved properties for manure amendments. In this study, zeolite at all treatment levels also reduced extractable P in samples at the end of trials by over one-half. Considering the recognized need to sequester P in manure, it would be worthwhile to examine the underlying chemistry of adding different forms of zeolite to manure. Zeolites which reversibly binds ammonium and permanently sequesters P would be good candidates for an amendment for the on-farm treatment of manures.

CONCLUSIONS

The results of this study indicate that both alum and zeolite treatment of dairy slurry can reduce ammonia volatilization. Alum added at a rate of 2.5% by weight reduced ammonia volatilization by nearly 60% by reducing the pH of the slurry to less than 5. Another benefit of alum is a marked reduction in soluble P due to the formation of low solubility Al-phosphate compounds. Disadvantages of alum include the potential for excess soluble Al if too much alum is added and the physical difficulties from effervescence. Excess alum should not be added because of added cost, and because excess levels of soluble aluminum should be avoided.

Zeolite also has the potential for reducing ammonia volatilization by sequestering ammonium-N on exchange cites. An addition of 6.25% zeolite resulted in a 50% reduction in ammonia volatilization. An additional potential advantage is that zeolite bound ammonium is a good slow-release N source for plants. In this study, zeolite at all treatment levels reduced extractable P in samples at the end of trials by over one-half, although

Table 5. The quantity of soluble aluminum in solutions of manure dissolved in calcium chloride, potassium chloride, or water relative to the mass of the dissolved manure. Measurements were made for manure sampled at the start and the end of individual trials.

	Extractable aluminum (mg/g) at start						Extractable aluminum (mg/g) at end					
	$CaCl_2$		KCl		Water		$CaCl_2$		KCl		Water	
Treatment	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE	Mean	SE
0.4% Alum	0.00	0.07	0.01	0.07	0.01	0.07	0.04	0.20	0.04	0.20	0.05	0.20
1% Alum	0.00	0.07	0.01	0.07	0.01	0.07	0.04	0.20	0.03	0.20	0.03	0.20
2.5% Alum	0.23	0.04	0.31	0.04	0.24	0.04	0.52	0.10	0.76	0.10	0.55	0.10
6.25% Alum	3.51	0.05	4.21	0.05	3.85	0.05	13.25	0.14	15.56	0.14	13.89	0.14
Control	0.00	0.02	0.00	0.02	0.00	0.02	0.01	0.07	0.02	0.07	0.01	0.07
0.4% Zeolite	0.00	0.07	0.00	0.07	0.00	0.07	0.02	0.20	0.01	0.20	0.01	0.20
1% Zeolite	0.01	0.07	0.00	0.07	0.00	0.07	0.01	0.20	0.02	0.20	0.01	0.20
2.5% Zeolite	0.01	0.04	0.00	0.04	0.01	0.04	0.01	0.10	0.03	0.10	0.02	0.10
6.25% Zeolite	0.02	0.05	0.01	0.05	0.01	0.05	0.04	0.14	0.03	0.14	0.05	0.14

the precise mechanism for this reduction in P remains obscure. No adverse physical effects were observed with zeolite amendments.

The use of alum or zeolite as on-farm amendment to dairy slurry offers the potential for reducing ammonia emissions and soluble P in dairy slurry.

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