Influence of Soil Amendments on In-vitro Ammonia Volatilization From Cattle Manure

Y. Shi, Graduate Student, West Texas A&M University
David B. Parker, Assistant Professor, West Texas A&M University
N. Andy Cole, USDA-ARS
Joey E. Mehlhorn, Assistant Professor, West Texas A&M University
Brent W. Auvermann, Assistant Professor, Texas A&M Research and Extension Center
L. Wayne Greene, Professor, Texas A&M Research and Extension Center and WTAMU

ABSTRACT

A laboratory study was conducted to evaluate soil amendments for reducing ammonia emissions from open-lot beef cattle feedyards. A mixture of 1550 g of soil, 133 g of feces, and 267 g of urine was placed into sealed plastic containers of dimensions 20 cm x 20 cm x 12 cm depth. Using a vacuum system, clean air at a rate of 3.2 L/min was passed over the soil-manure surface and ammonia was trapped by bubbling the air through dilute hydrochloric acid. Treatments consisted of a blank (soil with no manure), control (soil-manure mixture with no amendment), 4500 kg/ha $Al_2(SO_4)_3$ (alum), 9000 kg/ha alum, 375 kg/ha commercial product for reducing ammonia emissions (CP), 750 kg/ha CP, 4500 kg/ha calcium chloride ($CaCl_2$), 9000 kg/ha $CaCl_2$, 9000 kg/ha brown humate, 9000 kg/ha black humate, 1 kg/ha of the urease inhibitor N-(n-butyl)-thiophosphoric triamide (NBPT), and 2 kg/ha NBPT. There were four replications of each treatment. Ammonia emissions were monitored for 21 days following application of the amendments. Cumulative ammonia emissions after 21 days, expressed as a percentage of the control, were 0.4% for the blank, 8.5% for 4500 kg/ha alum, 1.7% for 9000 kg/ha alum, 73.6% for 375 kg/ha CP, 68.2% for 750 kg/ha CP, 28.8% for 4500 kg/ha $CaCl_2$, 22.5% for 9000 kg/ha $CaCl_2$, 32.4% for 9000 kg/ha brown humates, 39.8% for 9000 kg/ha black humates, 35.9% for 1 kg/ha NBPT, and 34.4% for 2 kg/ha NBPT. Results of these experiments suggest that ammonia emissions from open feedlots can be significantly reduced using chemical additives, but the costs may be prohibitive. Environmental impacts from the amendments should be evaluated before use in a commercial setting.

INTRODUCTION

Beef cattle producers face many challenges as the result of increased public concerns about effects of agricultural practices on the environment. Concerns about excessive nutrient accumulation in beef cattle feedyards stem from the fact that imports of elemental nutrients in purchased feeds are greater than nutrient exports in beef cattle products. Significant losses of nitrogen from feedyards occur by volatilization from urine and feces on the pen surface. In recent years, there has been a growing concern for the need to decrease the emissions of these and other gases produced by livesto ck and their waste products. Many countries in Europe already have regulations limiting the amounts of ammonia emissions from concentrated animal feeding operations. This concern results from studies indicating that these gases have the potential to contribute to the greenhouse effect, acid rain, and/or stratospheric ozone depletion. In addition, emissions of ammonia and oxides of N and S have been implicated as potential contributors to fugitive dust emissions, especially PM-10 and PM-2.5 particulates (Morse, 1996a; Morse, 1996b). It has been estimated that as much as 50% of feed N is lost as ammonia (Bierman, 1995). Research is needed to determine actual amounts of N lost to the environment, and to develop management procedures that will decrease these losses. The purpose of this research was to investigate the performance of several amendments for reducing ammonia emissions from a simulated feedlot surface.

MATERIALS AND METHODS

A mixture of soil, feces, and urine were placed into plastic containers of dimensions 20cm x 20cm x 12cm depth. There were 12 treatments, with four containers per treatment, for a total of 48 containers. The first treatment was the blank, in which only 1550g of soil was placed into the container. For all the other 11 treatments, 1550g of soil, 133g of feces, and 267g of urine were mixed then placed in the containers to simulate feedlot conditions. Amendments were added to the chambers at the following rates:

    Treatment 1: Soil Blank (soil only)
    Treatment 2: Control (Soil + manure without amendments)
    Treatment 3: Aluminum Sulfate 18 g/container, 4500 kg/ha (2 t/acre)

Treatment 4: Aluminum Sulfate 36 g/container, 9000 kg/ha (4 t/acre)
Treatment 5: Commercial product 1.5 g/container, 375 kg/ha (0.17 t/acre)
Treatment 6: Commercial product 3 g/container, 750 kg/ha (0.34 t/acre)
Treatment 7: Calcium Chloride 18 g/container, 4500 kg/ha (2 t/acre)
Treatment 8: Calcium Chloride 36 g/container, 9000 kg/ha (4 t/acre)
Treatment 9: Brown Humate 36 g/container, 9000 kg/ha (4 t/acre)
Treatment 10: Black Humate 36 g/container, 9000 kg/ha (4 t/acre)
Treatment 11: NBPT 4 mg/container, 1 kg/ha
Treatment 12: NBPT 8 mg/container, 2 kg/ha

Each chamber was connected to an ammonia collection trap containing 100 ml of 0.9 M hydrochloric acid. All of the acid traps were connected with plastic tubing to a large plastic container filled with water. The large container was connected to a vacuum pump (1 hp ShopVac) to control the airflow in the experiment chamber. The vacuum pump was adjusted for a total air flow rate of 153 L/min, or 3.2 L/min for each container. This corresponds to a linear air velocity of about 0.2 m/minute (0.007 mph) across the soil-manure surface, or a fresh air turnover rate of 1 turn per minute. The acid was changed every 24 hours for the first week and every 48 hours for the next two weeks.

Soil/manure mixture samples were collected and analyzed for moisture content and total nitrogen at the completion of the 3-week period. The pH of the soil/manure mixture was also measured at the completion of the experiment on two parts water to one part soil by weight. Acid samples were analyzed for total nitrogen by automated procedures. The results for each treatment were compared to test the effects of different amendments. Statistical analyses were performed using LSD comparisons (t-tests) using the SPSS Version 7.0 software package.

RESULTS AND DISCUSSION

Of the amendments evaluated, the alum (aluminum sulfate) was most effective in reducing ammonia emissions (Table 1). The 9000 kg/ha alum treatment reduced ammonia emissions to 1.7% of the control. Calcium chloride was also an effective ammonia emission reducer. Humate and NBPT were not as good, but they did reduce some ammonia volatilization. The commercial product reduced some ammonia emissions, but was not as effective as the other products.

The two alum treatments had the lowest soil pH at the completion of the experiments (Table 2). Calcium chloride, humates and the commercial product also had a lower pH than the control. It appears that pH is directly related to the ability of some additives to reduce ammonia emissions. The NBPT group had a similar pH as the control group.

The volatilization of ammonia is partially controlled by the surface pH of the soil. The major reactions of ammonia loss are:

$$CO(NH_2)_2 + H^+ + 2H_2O \Leftrightarrow 2 NH_4^+ + HCO_3^-$$
$$NH_4^+ \Leftrightarrow H^+ + NH_3 \qquad pKa = 9.3$$
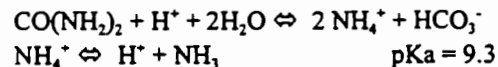
The first reaction is the process of ammonification. In this reaction, urea is hydrolyzed and produces ammonium ion. This reaction is catalyzed by the activity of urease. Hydrogen ion is a reagent, so low pH is a favorable condition for this reaction. In the second reaction, ammonium ion is converted to ammonia that can release from the manure. In this reaction, hydrogen ion is a product, so low pH will make the equilibrium move to the left side, inhibiting the production of ammonia and reducing ammonia volatilization.

Thus, low pH has two opposite effects on ammonia volatilization, but the second one is the major concern for ammonia emission. The aluminum ion (Al^{3+}) has a high cation exchange capacity, and it can function as a cation exchange competitor of hydrogen ion at the cation exchange site. It can replace the hydrogen ion on the cation exchange site and thus release the hydrogen ion into the soil solution. The soil pH will decrease as the concentration of hydrogen ions increases. Aluminum ion can also lower the soil pH by its hydrolysis:

$$Al^{3+} + H_2O = Al(OH)^{2+} + H^+$$
$$Al(OH)^{2+} + H_2O = Al(OH)_2^+ + H^+$$
$$Al(OH)_2^+ + H_2O = Al(OH)_3 + H^+$$
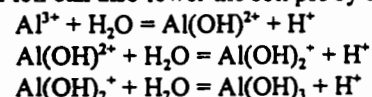
Because alum has both a strong cation exchange and hydrolysis capacity, it can strongly acidify the soil and thus reduce ammonia volatilization.

The calcium ion also has the same effects of cation exchange and hydrolysis. But the calcium ion has a bigger radius and less positive charge than the aluminum ion, so it is less powerful in cation exchange. Also, because the hydrolysis products of calcium ion ($Ca(OH)^+$ and $Ca(OH)_2$) are more soluble than the products of alum hydrolysis, the calcium ion is not as strong in hydrolysis effect as the aluminum ion. However, in addition to cation exchange and hydrolysis effects, the calcium ion can also react with the bicarbonate ion produced by urea hydrolysis:

$$Ca^{2+} + HCO_3^- = CaCO_3 - H^-$$
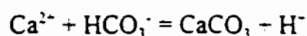
This reaction can also release a hydrogen ion, thus lowering the soil pH. Calcium carbonate ($CaCO_3$) is relatively insoluble, thus the reaction is prone to move to the right side and produce hydrogen ions. Because the soil we used in this experiment is a calcareous soil, there was an appreciable quantity of calcium ions already present. The addition of calcium ions in this experiment did not have much effect on the calcium concentration in the soil. Also in this kind of calcareous soil, the calcium, carbonate and bicarbonate ions form a buffering system, preventing dramatic pH change. The reactions are as below:

$$Ca^{2+} + HCO_3^- \Leftrightarrow CaCO_3 + H^+$$
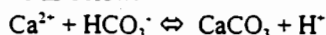
If the concentration of the hydrogen ion is high enough, it will react with calcium carbonate to produce calcium ion and bicarbonate ion, thus reducing the rate of pH drop.
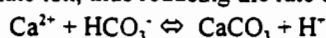
$$Ca^{2+} + HCO_3^- \Leftrightarrow CaCO_3 + H^+$$
$$K = K_{a2}/K_{sp} = constant$$

The calcium in the soil thus functions at the same time as a buffer against pH rise or drop. That is the main reason why the pH of the calcium-added soil is higher than the alum-added soil and lower than that of others. This is also the reason why the reduction in ammonia emissions with calcium chloride is not as great as that of alum.

Humate is a common substance found all over the world. It is the end product of the biological and chemical breakdown of the humic materials in prehistoric periods. It is mainly composed of organic carbon, humic acid and fulvic acid. Humic and fulvic acids are very important in humates' function in reducing ammonia emissions in the experiment. Both the humic acid and the fulvic acid are organic acids. Their active groups may be carboxylic acids and phenolic acids. Thus, the humate can be used as a soil amendment to lower the pH and acidify the soil. The ammonia volatilization will be reduced as the pH decreases. The final pH of the humate treatments is similar to that of the calcium treatments. The two types of humates did not show much difference in their ability of lowering soil pH. Humic acid has a dark brown to black color. It is more abundant in black humate. Fulvic acid has a yellow to red color, so it is more abundant in brown humate. In the present experiment, brown humate had a greater effect in reducing ammonia volatilization. This can be explained from the water holding ability of the two materials. The moisture content of the brown humate treatment is lower than that of the black humate treatment. A higher moisture content is advantageous to ammonia volatilization. When the moisture content is close to zero, the ammonia volatilization rate is also close to zero. The black humate has a greater water holding capacity, so its ammonia volatilization is more than that of the brown humate group. Humate can increase the buffering capacity of the soil, thus reducing the rate of pH change and ammonia release. Another benefit of humate is that it has a very high ion exchange capacity and chelating ability. The ammonium ion can attach to the surface of humate or be chelated by it (because the ammonium is very similar to metal ion in properties). As the concentration of ammonium ions in the soil solution decreases, the concentration of ammonia in the soil solution is also reduced, resulting in a reduced rate of ammonia volatilization.

The NBPT is an enzyme whose function is to inhibit the activity of urease. It binds to the enzyme (probably at the nickel ion at the enzyme) and inactivates it. Less urea is converted to ammonium ions, so the concentration of ammonium ion in the soil solution is not as high, reducing ammonia volatilization. Because NBPT works as a catalyst for biochemical reactions, the amount of the enzyme present is not critical to determine its effect on volatilization provided that the amount is already enough to work. In this experiment, if the amount of the enzyme in any of the two treatments was deficient, then they should have had different rates of reaction. However, they showed similar reaction rates. Thus, the amount of enzyme was sufficient for the reaction. NBPT works as a catalyst in the reaction, it is not a reagent. That is why adding additional NBPT did not decrease ammonia emission rates after an adequate amount had already been added. It is possible that NBPT can be applied at less than 1 kg/ha with the same desired effect.

ECONOMIC CONSIDERATIONS

The costs of the amendments delivered to the feedyard are presented in Table 3. These costs do not include labor or expenses for spreading the materials on the feedyard surface. We have yet to determine how often the amendments will have to be applied, so we calculated costs based on two scenarios to give a range of anticipated costs. The first scenario assumes one application at the beginning of the feeding period. The second scenario assumes application every 21 days, or six applications in a 120 day feeding period.

It is difficult to compare the costs of the amendments because each amendment performed differently in reducing ammonia emissions. In an attempt to compare the "relative cost" of each amendment, the cost per head in Table 3 was divided by the percentage of ammonia emission reduction. Relative cost for each treatment per percentage of ammonia emission reduction was ranked from lowest to highest as follows: 1) 1 kg/ha NBPT; 2) 2 kg/ha NBPT; 3) 375

114

kg/ha CP; 4) 750 kg/ha CP; 5) 4500 kg/ha CaCl₂; 6) 4500 kg/ha alum; 7) 9000 kg/ha CaCl₂; 8) 9000 kg/ha alum; 9&10) brown and black humate.

CONCLUSIONS

We demonstrated in a laboratory study that ammonia emissions from a simulated feedlot surface can be significantly reduced using additives. Ammonia emissions were reduced to as little as 1.7% of the control. Costs for the amendments, if applied only once at the beginning of the feeding period, ranged from as little as $0.12 to as much as $5.53 per head. While these amendments may have some promise in the future, additional investigations are necessary to determine 1) how often the amendments must be applied if a field setting, 2) if there are any adverse environmental effects from using the additives in a feedlot setting, and 3) if there are any adverse animal health or animal performance effects.

REFERENCES

Morse, D. 1996a. Understanding fugitive dust and ammonia emissions. Proc. 1996 Nat. Poultry Waste Management Symposium, pp. 19-23.
Morse, D. 1996b. Impact of environmental regulations on cattle production. Journal of Animal Science 74:3103-3111.
Bierman, S.J. 1995. Nutritional effects on waste management. MS Thesis, University of Nebraska, Lincoln, NE, June, 1995.

Table 1. Total ammonia volatilized over the 21-day experiment.

Treatment	Ammonia-N (mg)		% of Control	Rank
	Mean	Std. Dev.		
Blank (soil only)	17.2 a	1.5	0.4	
Control (soil with manure, no amendment)	4000 b	267	100	
Alum (4500 kg/ha)	240.2 c	241	8.5	2
Alum (9000 kg/ha)	67.2 a	26.8	1.7	1
Commercial Product (375 kg/ha)	2946 d	112	73.6	10
Commercial Product (750 kg/ha)	2728 d	204	68.2	9
Calcium Chloride (4500 kg/ha)	1151 ef	58	28.8	4
Calcium Chloride (9000 kg/ha)	899 f	99	22.5	3
Brown Humate (9000 kg/ha)	1296 eg	234	32.4	5
Black Humate (9000 kg/ha)	1590 h	169	39.8	8
NBPT (1 kg/ha)	1435 gh	91	35.9	7
NBPT (2 kg/ha)	1376 egh	297	34.4	6

Means with different letters are signifantly different at $\alpha=0.05$.

Table 2. Mean pH and moisture content of soil-manure mixture at the completion of the experiment.

Treatment	pH	Moisture Content (% dry weight basis)
Blank (soil only)	6.83	1.9
Control (soil with manure, no amendment)	7.55	8.9
Alum (4500 kg/ha)	5.98	9.2
Alum (9000 kg/ha)	4.20	8.9
Commercial Product (375 kg/ha)	7.12	6.9
Commercial Product (750 kg/ha)	7.39	9.0
Calcium Chloride (4500 kg/ha)	6.99	8.2
Calcium Chloride (9000 kg/ha)	6.85	8.3
Brown Humate (9000 kg/ha)	7.06	6.7
Black Humate (9000 kg/ha)	7.10	7.2
NBPT (1 kg/ha)	7.52	6.0
NBPT (2 kg/ha)	7.58	7.3

Table 3. Treatment application costs for the various amendments. Costs include materials and shipping to the feedyard, but do not include cost of spreading at the feedyard. All costs are for a stocking density of 14 m² per animal.

| Treatment	Amendment	Rate	Cost if applied once at beginning of feeding period ($/head)	Cost if applied six times during the feeding period ($/head)
1	None (Blank)	NA	NA	NA
2	None (Control)	NA	NA	NA
3	Aluminum Sulfate	4500 kg/ha	1.81	10.86
4	Aluminum Sulfate	9000 kg/ha	3.62	21.72
5	Commercial Product	375 kg/ha	0.72	4.32
6	Commercial Product	750 kg/ha	1.44	8.64
7	Calcium Chloride	4500 kg/ha	1.48	8.88
8	Calcium Chloride	9000 kg/ha	2.97	17.82
9	Brown Humate	9000 kg/ha	5.53	33.18
10	Black Humate	9000 kg/ha	5.53	33.18
11	NBPT	1 kg/ha	0.12	0.72
12	NBPT	2 kg/ha	0.24	1.44

116
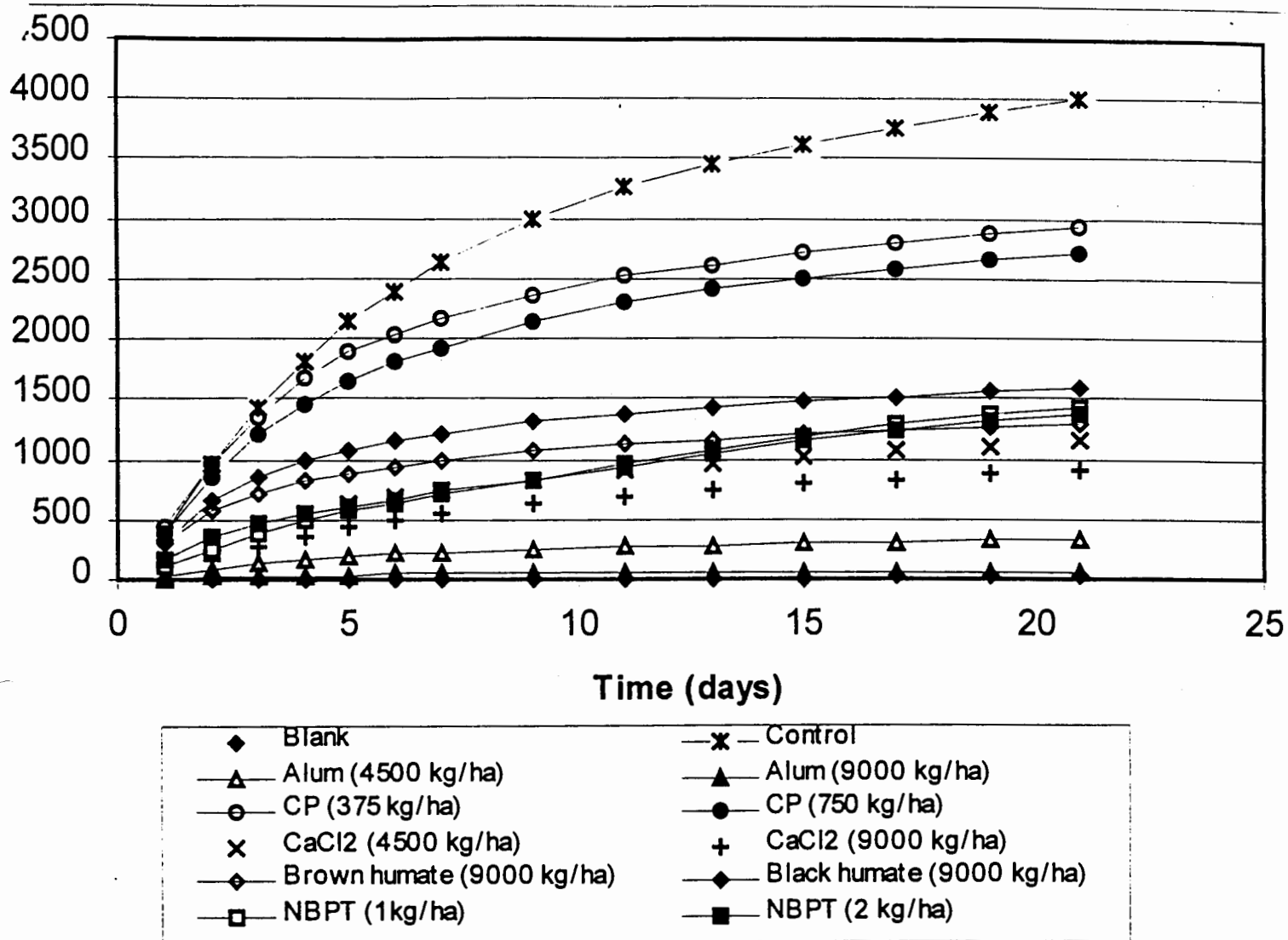
Figure 1. Cumulative ammonia emissions from manure-soil mixtures with various amendments.