Inexpensive Alternatives to Alum for Reducing Ammonia Emissions and Phosphorus Runoff from Manure

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Phosphorus Runoff from Poultry Litter

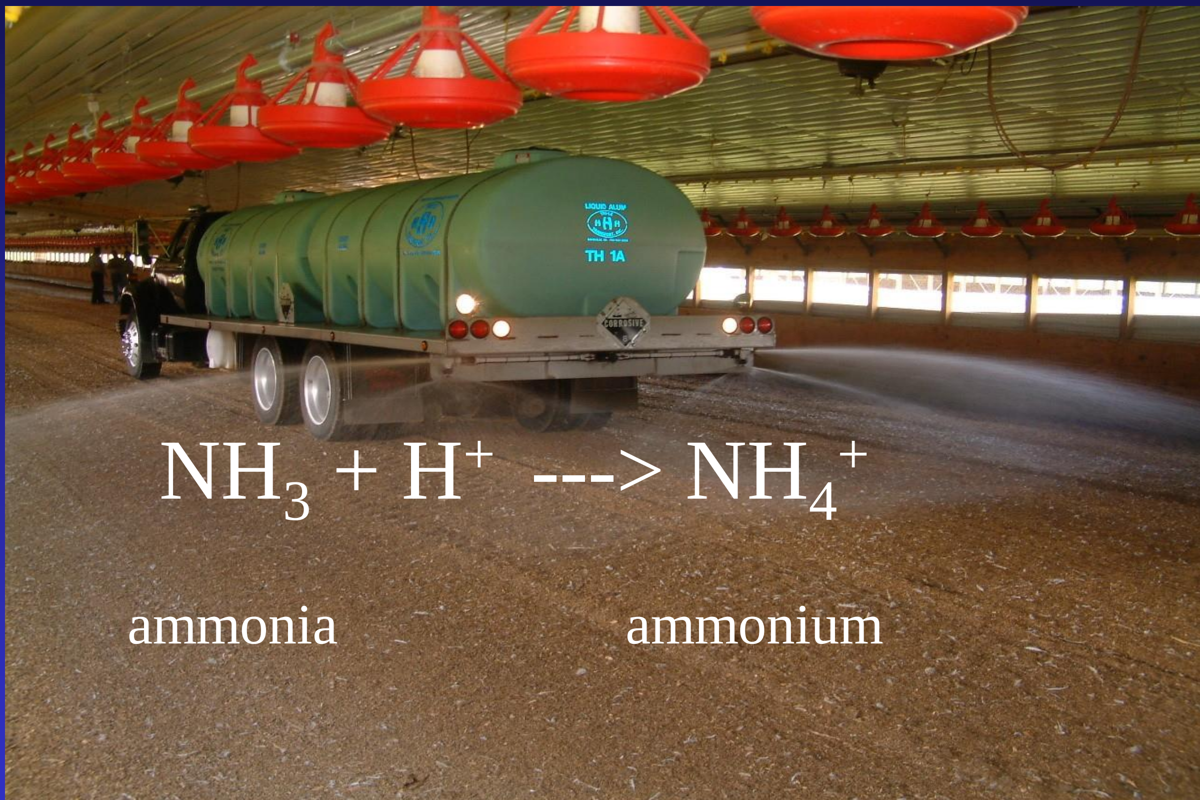
- The majority (80-90%) of P in runoff from pastures and no-till crops fertilized with manure is dissolved reactive P, which is the form most available for algal uptake.

- In the 1990s we found that Al, Ca, and Fe amendments could be used to reduce water soluble P in poultry litter by orders of magnitude (Moore and Miller, 1994) .

- Aluminum sulfate (alum) additions to poultry litter have also been shown to reduce P runoff from litter by 87% from small plots and by 75% from small watersheds (Moore et al., 1999; Shreve et al., 1995; Huang et al., 2016).

- Alum was also found to reduce ammonia emissions from poultry litter better and was more cost-effective than other products used for ammonia control (Moore et al., 1995, 1996).

Reducing ammonia loss and P runoff with alum



- Alum is added between flocks to the litter. It provides protons, which shifts the NH_3/NH_4^+ equilibria toward NH_4^+.
- Lower litter pH also reduces pathogens (*Campylobacter* and *Salmonella*) in litter (Lines, 2002).
- Aluminum in alum reacts with P to make an insoluble aluminum phosphate mineral, which results in lower P leaching and runoff.

Economic benefits of alum

- Alum applications to litter in commercial broiler houses reduced ammonia fluxes from litter by 70% and reduced in-house ammonia concentrations (Moore et al., 2000).
- Alum additions resulted in heavier birds, improved feed conversion, lower condemnation and lower mortality (Moore et al., 2000). This is due to lower ammonia and fewer pathogens.
- Alum use also lowers the ventilation requirements in broiler houses, particularly in cooler months. This results in significantly lower propane and electricity use (Moore et al., 2000) and lower CO_2 emissions (Eugene et al., 2015).
- Higher N content in litter results in higher crop yields with alum (Moore and Edwards, 2005; Shreve et al., 1995).
- These benefits make alum cost-effective (Moore et al., 1999).

Long-term alum research

- Two 20 year studies on the effects of treating poultry litter with alum from 1995 to 2015; a paired watershed study and a small plot study that utilized 52 plots with 13 treatments.
- The results were published in ten publications (Huang et al., 2016; Moore et al., 1998, 1999, 2000; Moore and Edwards, 2005, 2007; Moore, 2011; Savin et al., 2015; Tomlinson et al., 2007, 2015).

Results from long-term studies on alum

- Forage yields were significantly higher with alum-treated litter than normal poultry litter or ammonium nitrate.
- Phosphorus uptake by forage was not affected by alum.
- Exchangeable Al in soil, Al runoff, and Al uptake by plants was not affected by the use of alum.
- Concentrations of P, As, Cu, Zn, and estrogen were lower in runoff water with alum-treated litter than normal litter.
- Phosphorus leaching was significantly reduced with alum.
- Soil microbial biomass and enzyme activities were generally improved by alum additions to litter.

Alum use by the poultry industry

- This technology was patented (Moore, 1997; 1999a, b, c, d) and licensed to General Chemical Corporation, which markets poultry grade alum as "Al⁺Clear".

- Because of the economic benefits of this best management practice over one billion chickens are grown with alum each year in the USA.

Acceptance of alum as a BMP

- The USDA Natural Resources Conservation Service has a Conservation Practice Standard for litter amendments like alum, hence, cost-sharing is available to farmers for this practice.
- Likewise, many of the biggest poultry companies in the U.S. provide cost-share for poultry producers who use alum.
- However, there are approximately 9 billion broilers raised annually in the U.S., yet only one billion are grown with alum.
- The question is, if alum has so many benefits, why doesn’t everyone use it?

Why not use an industrial waste stream?

- The price of alum has increased significantly in the past five years and cost-sharing from NRCS or the integrator is not always available. Plus the economic benefits (particularly better feed conversion) helps the integrator a lot more than the grower.

- When we did the original alum work in the 1990s we spent a lot of time trying to find a cheaper industrial residue or "waste product" to use to precipitate P and reduce ammonia loss, but none were suitable.

- We tested red mud and brown mud, which are waste streams from aluminum mining that are left over from the Bayer process, which uses sodium hydroxide to extract aluminum from bauxite. They had little effect on soluble P and were buffered at a high pH, which would increase ammonia loss.

- Other wastes streams tested were loaded with toxic metals.

Alum mud

- There is another method that is used to make alum. In this second method, bauxite is reacted with sulfuric acid for a long period in a big reactor. The solids are then allowed to settle and the liquid on top, which is liquid alum, is either sold or dried to make dry alum.

- The solids that settle out are referred to as "alum mud", which is a waste material. It is landfilled at a cost of about $30/wet ton.

- Alum mud is acidic because it has been reacted with sulfuric acid, plus it has a very high aluminum content. However it is not acidic enough alone to be a litter amendment. When acid is added to it, the mixture becomes wet and very sticky and difficult to handle.

- Experiments were conducted on different mixtures using the chemicals available at these plants (alum mud, bauxite, sulfuric acid, liquid alum and water) to try to find a good amendment.

Amounts of various components (grams) in different mixtures from “Quick & Dirty Studies”

Mixture	alum mud	bauxite	sulfuric acid	liquid alum	Water
1	200	15	135	0	0
2	185	30	140	0	0
3	170	45	145	0	0
4	215	0	130	0	0
5	185	15	125	30	0
6	0	215	195	0	0
7	110	105	160	0	0
8	155	45	135	30	0
9	0	200	180	30	0
10	175	0	95	90	0
11	140	0	75	150	0
12	145	30	100	95	0
13	0	0	7.5	74.7	17.9
14	115	0	50	210	0
15	140	60	135	35	0
16	85	85	120	90	0

Quick & Dirty Results

- Almost all of our mixtures resulted in exothermic reactions. Sometimes they were a bit violent. Most mixtures would harden within 4-5 minutes of adding sulfuric acid.

- Some mixtures became as hard as granite. Although they are unsuitable as a litter amendment, we are going to try to patent these as a new construction material (replacement for concrete). Other mixtures resulted in a product that was similar to wet sticky mud, which would also be unsuitable for processing & handling.

- When just a little bit of bauxite (5-15%) is mixed with the right amount of alum mud (45-60%), then treated with sulfuric acid (35-50%), it results in a nice, dry, crumbly product that can be handled, bagged and easily spread in chicken houses.

- We compared the best mixtures to alum in a NH_3 lab study.

Laboratory Ammonia Volatilization Study

- 100 g fresh poultry litter was placed into 44 plastic containers. There were 11 treatments with 4 reps/treatment in RBD.
- Treatments were surface applied to litter without mixing. Most amendment rates were 4 g/100 g litter (~100 lbs/1,000 ft^2). This is a low rate, but it is typical of what is used by the industry.
- Ammonia-free air passed through containers and any ammonia exiting was trapped in boric acid traps which were titrated daily.
- At day 14, litter was analyzed for pH, EC, soluble metals, soluble P, and KCl-extractable ammonium.

Treatments

Control

4 g dry alum

8 g liquid alum (sprayed on with mister)

4 g of mixture 1 (57.1 % alum mud, 4.3% bauxite, 38.6% sulfuric acid)

4 g of mixture 2 (52.1 % alum mud, 8.5% bauxite, 39.4% sulfuric acid)

4 g of mixture 3 (47.2% alum mud, 12.5% bauxite, 40.3% sulfuric acid)

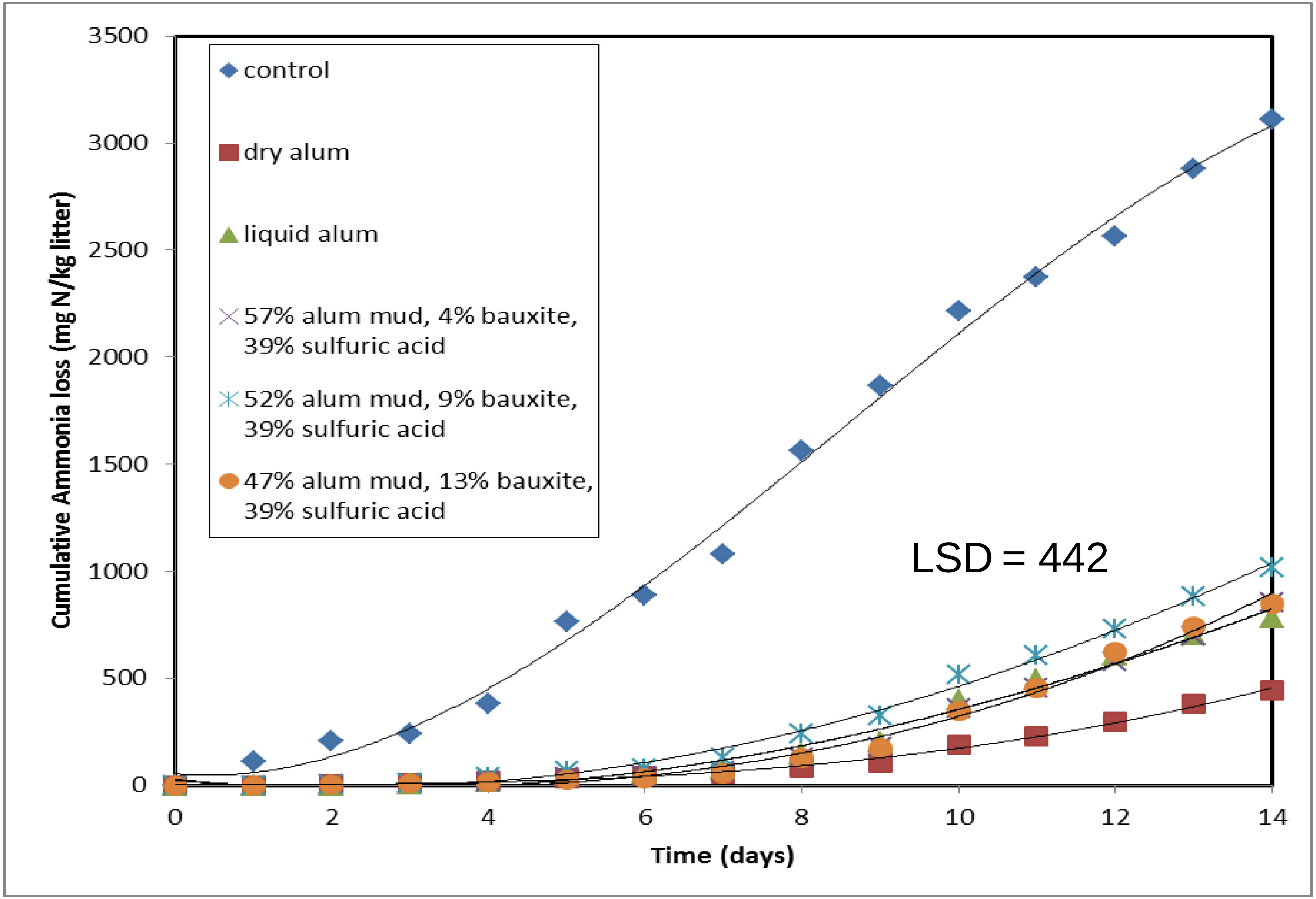
4 g of mixture 5 (52.1% alum mud, 4.2% bauxite, 35.2 % sulfuric acid, 8.5% liquid alum)

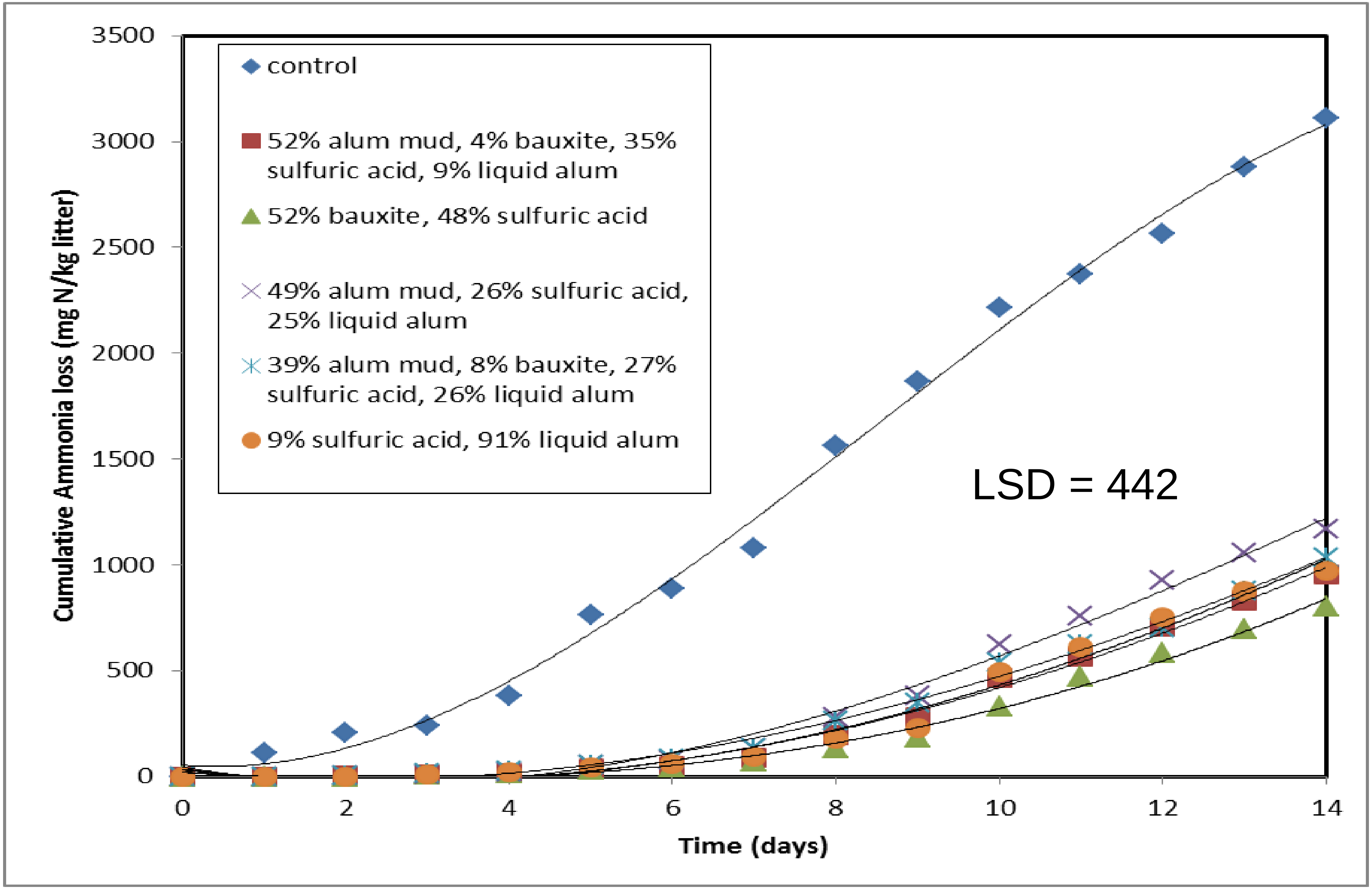
4 g of mixture 6 (52.4% bauxite, 47.6% sulfuric acid)

4 g of mixture 10 (48.6% alum mud, 26.4% sulfuric acid, 25% liquid alum)

4 g of mixture 12 (39.2% alum mud, 8.1% bauxite, 27% sulfuric acid, 25.7% liquid alum)

8 g of mixture 13 (9.1% sulfuric acid, 90.9% liquid alum, sprayed on with mister)


3500
3000
2500
2000
1500
1000
500
0
Cumulative Ammonia loss (mg N/kg litter)
0
2
4
6
8
10
12
14
Time (days)
control
dry alum
liquid alum
57% alum mud, 4% bauxite, 39% sulfuric acid
52% alum mud, 9% bauxite, 39% sulfuric acid
47% alum mud, 13% bauxite, 39% sulfuric acid
LSD = 442



control
52% alum mud, 4% bauxite, 35% sulfuric acid, 9% liquid alum
52% bauxite, 48% sulfuric acid
49% alum mud, 26% sulfuric acid, 25% liquid alum
39% alum mud, 8% bauxite, 27% sulfuric acid, 26% liquid alum
9% sulfuric acid, 91% liquid alum
LSD = 442
Cumulative Ammonia loss (mg N/kg litter)
3500
3000
2500
2000
1500
1000
500
0
0
2
4
6
8
10
12
14
Time (days)

Treatment	Litter pH in water	Cumulative NH_3 Loss in 14 days (mg N/kg)	KCl Extractable NH_4 (mg N/kg)	Water Extractable P (mg P/kg)	Water Extractable Zn (mg Zn/kg)
Control	8.89 a	3109 a	3300 e	1234 a	55.0 a
Dry Alum	7.97 c	440 c	5660 abcd	920 b	36.3 def
Liquid Alum	8.12 bc	782 bc	5620 bcd	656 e	34.5 ef
Mixture 1	8.13 bc	855 bc	6050 ab	862 bc	38.0 bcd
Mixture 2	8.20 bc	1016 b	6080 a	907 bc	40.5 b
Mixture 3	8.24 b	850 bc	5840 abc	735 de	37.3 cde
Mixture 5	8.19 bc	955 b	5920 abc	872 bc	38.8 bcd
Mixture 6	8.16 bc	802 bc	5980 ab	850 bc	38.6 bcd
Mixture 10	8.17 bc	1167 b	5320 d	934 b	39.3 bc
Mixture 12	8.26 bc	1032 b	5490 cd	816 cd	38.8 bcd
Mixture 13	8.05 bc	971 b	5770 abc	707 e	34.0 f
LSD 0.05	0.25	442	445	99.9	2.85

Conclusions

- All of the manure amendments resulted in significantly lower ammonia volatilization than the control (untreated litter).
- Ammonia volatilization was reduced by 62 to 73% with the 8 new manure amendments, which were not significantly different from liquid alum. Three were not different from dry alum.
- All of the amendments reduced water extractable P (WEP). Three of the new mixtures resulted in lower WEP than dry alum.
- The most promising products were simple mixtures of alum mud, bauxite and sulfuric acid.
- The potential impact of these new products could be enormous since they could be produced for less than half the price of alum.

U.S. Patent awarded for this technology

- We patented this technology (Moore, P.A. 2016. U.S. Patent 9,301,440) and USDA/ARS is currently seeking commercial partners interested in licensing this technology.

For more information on this study:

Moore, P.A., Jr. 2016. Development of a new manure amendment for reducing ammonia volatilization and phosphorus runoff from poultry litter. J. Environ. Qual. 45:1421-1429.

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