Spring 4-30-2018

Evaluation of CAFO Dairy Manure Treatment to Reduce Nutrient Transport

Jenna Laib
jlaib@bgsu.edu

Evaluation of CAFO Dairy Manure Treatment to Reduce Ammonia Transport

Jenna Laib

Honors Project

Submitted to the Honors College

Bowling Green State University in partial

Fulfillment of the requirements for graduating with

University Honors

April 30, 2018

Dr. W. Robert Midden, Advisor

Chemistry Department

Dr. Alexis Ostrowksi, Advisor

Chemistry Department

Abstract

Excess amounts of phosphorus and nitrogen flowing into Lake Erie from agricultural fields in Northwest Ohio has led to several harmful algal blooms (HABs). One potential source of those nutrients is manure applied to fields for fertilizer. Manure from confined animal feeding operations (CAFOs) is 95-98% water with only ~3% solids and nutrients, thus physical transportation is expensive relative to the value of the agricultural nutrients. Furthermore, once manure nutrients are applied to agricultural fields, they are relatively easily mobilized to waterways by precipitation. More than 800 lab-scale tests have been used to optimize the treatment of CAFO manure with cationic polymers and coagulant, which are commonly used in wastewater treatment plants, to sequester the nutrients as solids separated from water, thus reducing the weight by a factor of 20 and binding the nutrients in a form that greatly reduces its mobility in soils. Preliminary results are promising, showing that the runoff from the fields with the treated manure have significantly less phosphate levels compared to plots with untreated manure, as work is still being done for improving the results of the other nutrients. One of those nutrients is ammonia. This study is aimed at developing a strategy to increase the capture of ammonia and release slower and more consistently over time. Different strategies were tested, and the successful ones show improved capture of ammonia and slower release.

Background

The work performed in the lab has helped develop the idea for the honors project research. Hundreds of lab-scale tests have been performed for solid/liquid separation and nutrient binding in manure. The research group has determined that the best performing recipes use polymers NS 4375 and Zetag 8816 and coagulant AH 1010P. Various mixing methods and times were used to treat the manure with AH 1010P and polymers NS 4375 and Zetag 8816 to develop the optimal treatment protocol, which could be used in a wastewater treatment plant. Liquid fractions of separated manure were analyzed for nutrient content of dissolved phosphate, ammonia and nitrate+nitrite. Rain simulations were then conducted to analyze the release of nutrients and potential runoff from treated and raw manure in soil. So far, the results have been great for phosphate, but have not been as proficient in ammonia capture and release.

Our lab worked with the Village of Ottawa Wastewater Treatment to conduct a pilot test study at the Northwest Agricultural Research Station (NWARS) using eight small scale plots: two plots are controls, three plots were treated with raw manure and three plots were treated with treated manure. Each plot has two drainage tiles, a surface water tile and subsurface tile, which collect the runoff water and the water that is absorbed into the ground. The tiles run to a sample collection building. Automated water samplers are connected to the tiles in order to pull samples of the runoff water for nutrient analysis. Flow measurement devices measure the amount of water draining from the plots. These data are transmitted to the U.S. Geological Survey's Ohio Water Science Center via a cellular communications system and provided in real time via a web-based interface.

Introduction

Harmful algal blooms have become an increasing threat to water systems and ecosystems. This can be shown with the occurrence of harmful algal blooms (HABs) not only here in Ohio, but all across the country and the world. HABs occur when certain types of cyanobacteria grow excessively in lakes and rivers. This happens most commonly because of elevated levels of nutrients used to promote the growth of agricultural crops, especially phosphate. Not only do HABs impact the environment, but these harmful algae can also have a terrible effect economically and both of these impacts can have a massive devastation if this problem is not addressed.

One contributing factor to HABs is manure placed on agricultural fields to act as a fertilizer and the runoff that is associated with the manure (Mulbry et al, 2005). The nutrients in the manure can be washed away with rain and irrigation treatments, so instead of the crops utilizing the nutrients, the nutrients are carried away in runoff water. Rapid and timely information about manure nutrient content are needed to minimize the risks of phosphorus over-application and losses of dissolved P in runoff from fields treated with manure (Lugo-Ospina et al, 2005). The aim at looking into these factors are to optimize conditions for transforming dilute manure from Concentrated Animals Feeding Operations (CAFOs or "factory farms") into dewatered material that sequesters the nutrients in a form that serves as a "slow-release fertilizer". Dewatering dilute CAFO manure produces material that is much less expensive to transport and thus enables using it at those locations where it provides the greatest benefit rather than over applying it to local lands. Dairy manure is about 95-98% water and with water being dense, this causes an increase in price when transporting all that liquid for not the best value in terms of the nutrients. By extracting the water from the manure, farmers will be able to get twenty to forty times more nutrients than in the liquid form. Researchers have looked into ways in which the manure can be treated to minimize runoff of phosphorus and other nutrients, but maintaining a slow release that will allow nutrients to be available to fertilize crops (Dao & Daniel, 2002). The slower release of nutrients by this material compared to raw manure, at a rate that better matches uptake by crops, is expected to reduce the loss of nutrients to waterways. Raw manure applied to fields tend to leave the nutrients on the surface so when rains come, these nutrients are not bonded to anything so it creates runoff. However, with treated manure, the nutrients would be bound and there would be a slow-release effect when the nutrient release is more controlled thus not having as much runoff. If project goals are achieved, the value of the slow-release fertilizer produced would be high enough that its sale might produce a financial profit. A very low cost or even profitable process would provide a significant incentive for use thus achieving a substantial reduction in the adverse environmental impact of CAFO manure use.

An important aspect of using manure as fertilizer is determining the amount of nutrients that plants and crops need in order to grow and produce a strong yield. One nutrient that most crops need, especially corn, is nitrogen. However, looking at the nutrients in raw dairy manure, nitrate is barely present which means that raw manure alone cannot be used as a fertilizer (Gai et al., 2017). Farmers that are currently using raw manure as fertilizer have to supplement with other methods, usually commercial nitrogen fertilizer, because nitrate is insufficient and thus their corn yield will not be good (Saba et al., 2013). However, farmers have to be careful because some combinations of organic material do now mix well with chemicals and would not provide a good yield (Saba et al., 2013). Another important issue with using manure as fertilizer would be the odor that is produced. Ammonia volatilization occurs when ammonium in the soil is converted to ammonia because of pH; the ammonia is lost as a gas (Soils: part 5). Nitrogen is a part of ammonia so by capturing ammonia, nitrogen will be captured as well. Over half of the nitrogen content of manure can be in the form of ammonia which is readily lost to volatilization under hot, aerated conditions (Jokela et al., 2008). However, by capturing the ammonia the amount of gas produced will be reduced thus reducing the odor. Currently, ammonia emissions from agriculture are not directly regulated like phosphate and nitrate+nitrite are (Powell et al., 2015). Little research has been done on ammonia in regards to treated manure, but one article found that just by changing pH or how far down into the soil the treated manure is applied can significantly impact the amount of ammonia retained for an extended period of time (Costa et al., 2014). Ammonia does have some negative aspects to it and for these reasons it would be good to eliminate as much runoff as possible. Deposition of ammonia can cause eutrophication of surface waters, where phosphorus concentrations are sufficient to support harmful algal growth (Becker et al., 2014). Sensitive crops such as tomatoes, cucumbers, conifers, and fruit cultures can be damaged by over-fertilization caused by ammonia deposition if they are cultivated near major ammonia sources (van der Eerden et al, 1998). The deposition of ammonium on soils with a low buffering capacity can result in soil acidification or basic cation depletion (Becker et al., 2014). Ammonia needs to be involved in the treatment of manure, so making sure the ammonia is captured and released slowly is very important for this research.

Methods

Water Purifier System

The purified water system used for all testing and analysis is from the Direct-Q Water Purification System. The system resistivity is 18.2 MΩ•cm at 25 °C.

Liquid Polymer Solution Addition

Treatment of manure begins with liquid manure that is pulled from buckets after mixing to ensure the solids are uniformly suspended. The pH is measured and recorded and then the manure is placed under a Lovibond stir machine. The coagulant is added and the solution is mixed 10 minutes on the surface at 75 rpm and then 10 minutes on the bottom at 65 rpm. The pH is taken after these 20 minutes. Then the polymer is added and the solution is mixed for 10 minutes on the surface at 75 rpm and then 10 minutes on the bottom at 65 rpm. Once all is mixed, the solution is covered and allowed to sit overnight. The next day the solution is filtered and the solid “cake” dried while the filtrate is analyzed for pH, turbidity, volume and the nutrients ortho-phosphate, nitrate+nitrite and ammonia.

Some variations on this method were tested to determine if better ammonia capture could be achieved. Different anionic polymers were chosen to for the different tests – Pectin from citrus peel Galacturonic acid $\geq$ 74% (dried basis) from Sigma Life Science and Alginic aid sodium salt from brown algae with medium viscosity from Sigma Life Science were used. These polymers were prepared as a 1% solution purified water. The cationic polymer was 8816. In one group of tests, an anionic polymer was added to the raw manure and mixed then the cationic polymer was added and mixed until filtration. In another group of tests, the cationic polymer was added to the raw manure and mixed, then the anionic polymer was added and mixed before filtration. A third set of tests was conducted in which the cationic polymer was added to the raw manure, mixed and filtered and then the anionic polymer was added to the filtrate. Lastly, mixing the cationic and anionic polymers prior to their addition to the manure was tested. The cationic/anionic combination was mixed with manure followed by filtration. Samples were collected and analyzed for nutrient levels, especially ammonia, to determine if the photopolymers are capturing these nutrients.

Nutrient Absorption with Polymer Beads

Part of the research in the lab also involves making beads, instead of the traditional “cakes” using alginate and placing the alginate beads in samples of manure so they absorb the nutrients. These beads are placed into cups and raw, liquid manure solution is added. After 24 hours, samples of the remaining liquid are collected and analyzed for the concentration of the dissolved ammonia. The remaining concentration is compared to the starting concentration of the raw manure to determine the amount that is captured by the beads. This test was also done with a known concentration of an ammonia solution.

Rain Simulations

Another way the manure treatment is evaluated in the lab is through the use of rain simulations. After the solid manure cakes are allowed to dry, they ca be used in rain simulations. A test system consists of filter holders, Whatman 47 mm polyethylene filter holders filled with washed soil that has been sieved for both course and fine soil (to take out the impurities) that have filters in the bottom into glass jars. There are controls in which no manure of any kind is added, two where raw manure is mixed and the rest consist of "cakes" mixed into the soil. Purified water is added to each of the samples and over time the water will seep through the soil and runoff will be in the glass jars. The filtrate is collected, filtered and run through the Seal AQ+ machine where levels of phosphorous, nitrate+nitrite and ammonia are obtained.

Results

Liquid Polymer Solution Addition

Some of the different methods of mixing and the different polymers that were tested was beneficial. Using pectin and alginate versus the cationinc polymer that has been used previously (8816) has worked at capturing more of the ammonia, but there also has to be larger amounts used. Instead of the 30 mL of 8816 used, these polymers required about 100 mL. The same is true for the coagulant; instead of 2 mL of 1010P there would have to be about 4 mL of 1010P used. There were multiple ways in which these ratios were added and their effectiveness was evaluated. Some of the treatments contained treatment in which all three polymers (pectin, alginate and 8816) were used while there were tests were variants of only two polymers were used, for example a 8816/pectin mixture and a 8816/alginate mixture. For the coagulants, some different methods were dilutions of 1010P, smaller and larger amounts of 1010P. When both the polymer and coagulant were added at the same time, it did not work because it would form just a big clump and not mix with the manure well. When the anionic polymer was added and then the cationic and vice versa, the results looked varied. Some treatments and recipes worked better than others. One recipe that worked well was 4 mL of 1010P and 50 mL 8816/50 mL alginate likewise 4 mL of 1010P and 50 mL 8816/50 mL pectin. Making sure the ratio of polymer to coagulant is critical, otherwise it could clump up too much or not enough. Also, utilizing cationic and anionic polymers seemed to work better than just one or another.

Figure 1. Solid "cakes" manure left over after treatment and a drying period.

Nutrient Absorption with Polymer Beads

The bead style of this approach is also very promising. When the beads were placed in just a known dissolved ammonia concentration, after 24 hours there was about 20-22% of ammonia remaining in the solution. There was one group where there was about 8% of ammonia remaining in the solution. When the beads were placed in raw manure, with the dissolved ammonia concentration known, the uptake was much more efficient in which only about 2-5% of ammonia was remaining in the solution. The ammonia in the raw manure started at a much higher concentration (about 20 times higher) than the ammonia-only solution.

	Type of Gel Bead (5g)	Average Dissolved Ammonia Concentration after 24 hrs in 250mgN/L	Average Dissolved Ammonia Concentration of Raw Manure (mgP/L) in 10mL	Average Dissolved Ammonia Concentration of Manure (mgP/L) 24 hrs after bead addition	Average Percent Dissolved Ammonia Remaining
A1	1% Alginate in 0.1% Alum in 0.05M FeCl3	54.22			21.69%
C1	0.5% Alginate 0.5% Pectin in 0.05M FeCl3	53.99			21.59%
A2	1% Alginate in 0.1% Alum in 0.05M FeCl3		968.82	22.03	2.27%
B2	1% Alginate 0.05M FeCl3		968.82	22.11	2.28%
C2	0.5% Alginate 0.5% Pectin in 0.05M FeCl3		968.82	22.07	2.28%
A3	1% Alginate in 0.1% Alum in 0.05M FeCl3	52.4776			20.99%
B3	1% Alginate 0.05M FeCl3	52.2064			20.88%
C3	0.5% Alginate 0.5% Pectin in 0.05M FeCl3	52.171			20.87%
A4	1% Alginate in 0.1% Alum in 0.05M FeCl3		968.82	52.3452	5.40%
B4	1% Alginate 0.05M FeCl3		968.82	52.6215	5.43%
C4	0.5% Alginate 0.5% Pectin in 0.05M FeCl3		968.82	52.1684	5.38%
A5	1% Alginate in 0.1% Alum in 0.05M FeCl3	21.0649			8.43%
B5	1% Alginate 0.05M FeCl3	21.029			8.41%
C5	0.5% Alginate 0.5% Pectin in 0.05M FeCl3	20.9939			8.40%
A6	1% Alginate in 0.1% Alum in 0.05M FeCl3		968.82	21.2905	2.20%
B6	1% Alginate 0.05M FeCl3		968.82	21.3691	2.21%
C6	0.5% Alginate 0.5% Pectin in 0.05M FeCl3		968.82	21.4091	2.21%

Figure 2. The average dissolved ammonia before and after addition of beads in ammonia solution and raw manure.

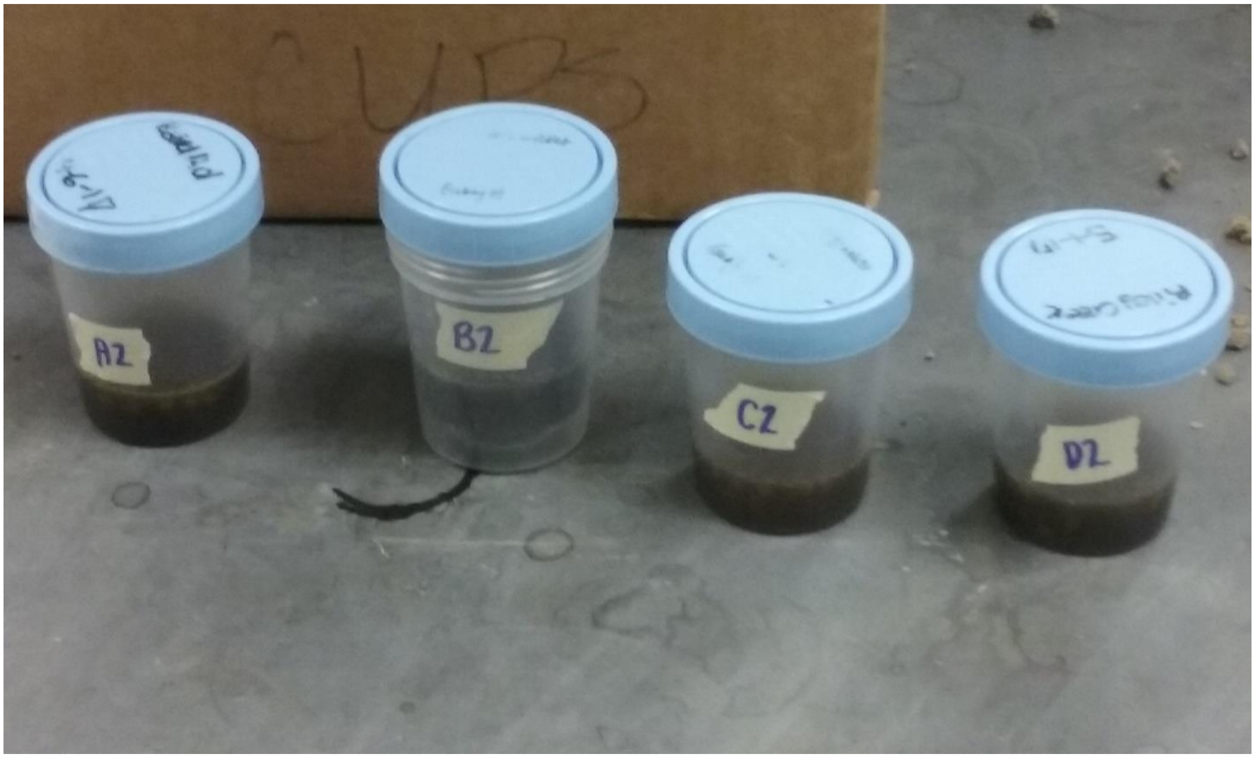

Figure 3. The ammonia absorption test with raw manure samples.

Figure 4. The polymer beads drying in a dish.

Figure 5. The polymer beads after they were made by dropping alginate in a $FeCl_3$ solution.

Rain Simulations

Comparing the results of a rain simulation from the original recipe showed that the original treatment was never very good at capturing high levels of ammonia. The new treatment was able to capture the ammonia better. The goal was to have higher amounts of ammonia to begin with and then have a longer period of release over time. Based on the new graph and results, this is can be seen to have been achieved to a certain extent. Take note of the y-axis range as well as before the new treatment, the maximum y-axis value is 8 mgN/L and with the new treatment the y-axis reached about 40 mgN/L. This also has a promising effect on the nitrate concentrations as well as there is more nitrate captured and released over time in this new treatment than previously.

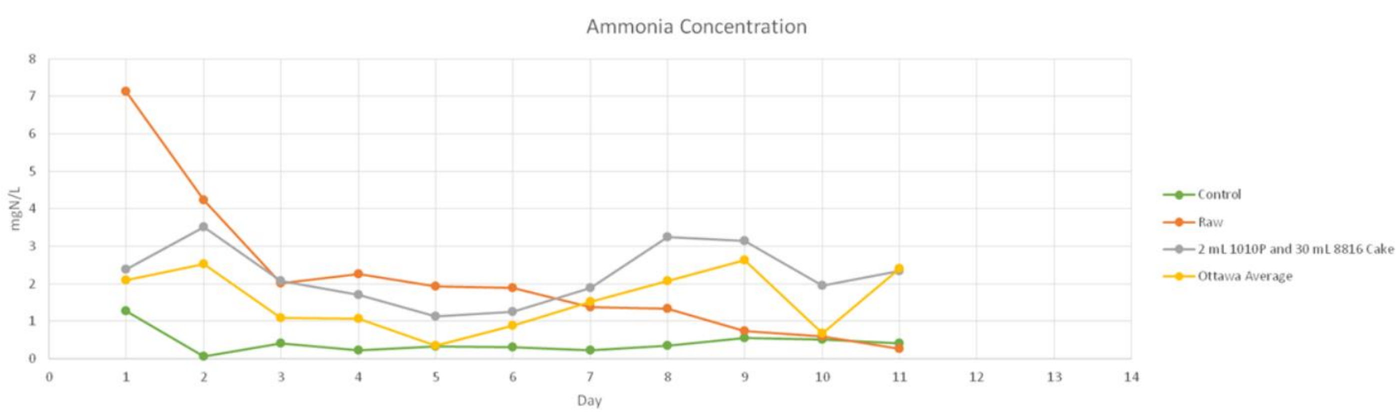

Figure 6. The concentration of ammonia released in Rain Simulation M over time. Note the scale.

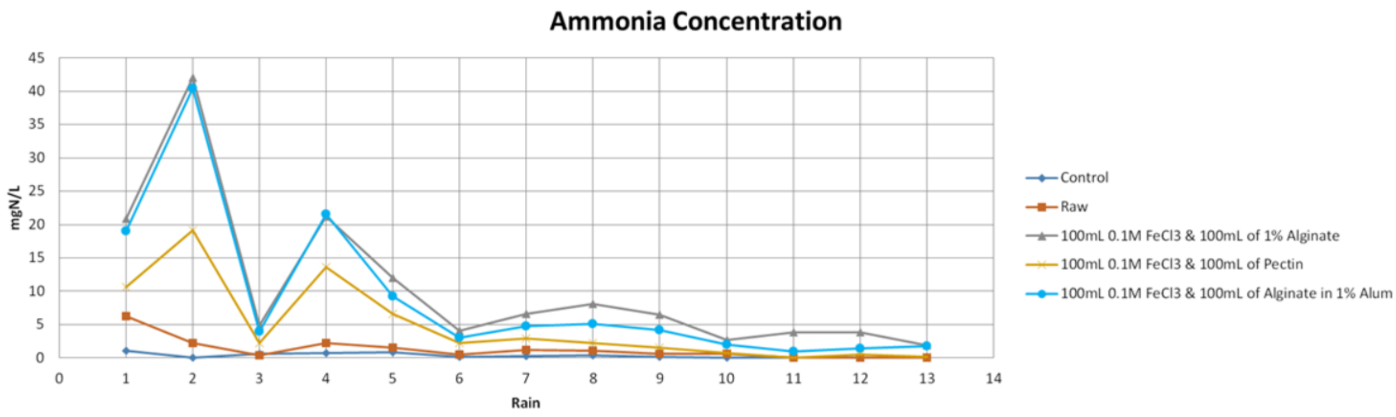

Figure 7. The concentration of ammonia released in Rain Simulation S over time. Note the scale.

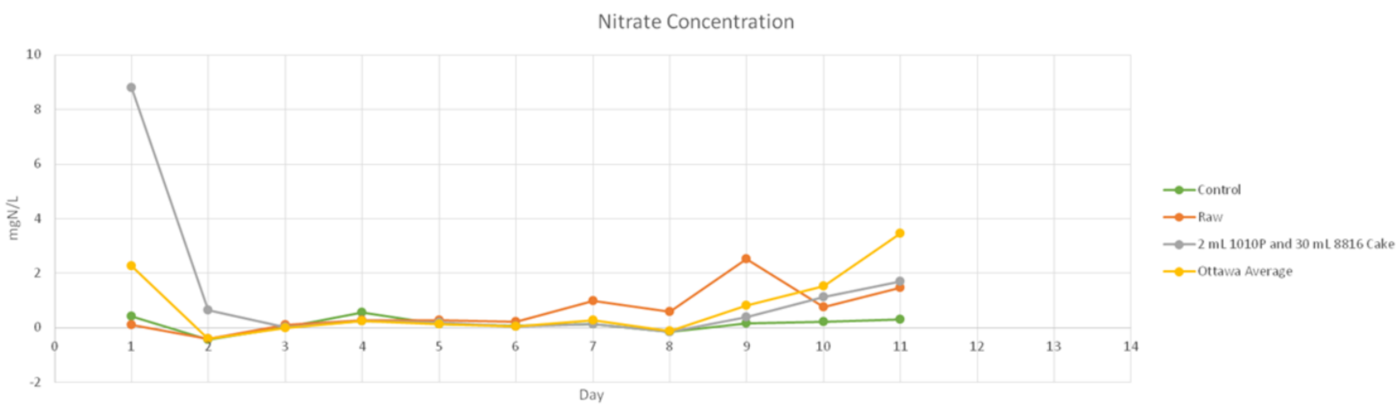

Figure 8. The concentration of nitrate released in Rain Simulation M over time. Note the scale.

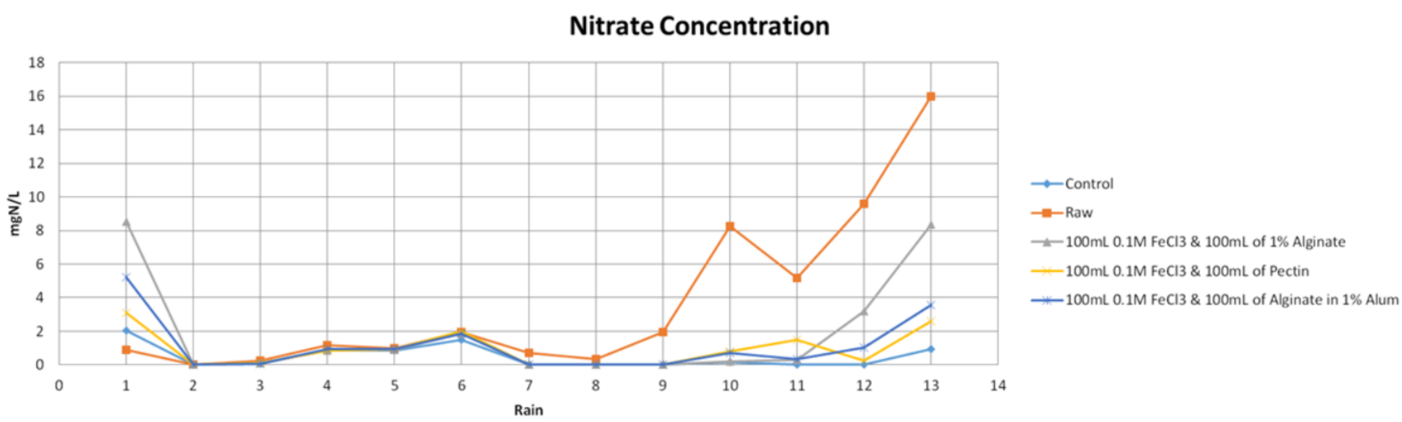

Figure 9. The concentration of nitrate released in Rain Simulation S over time. Note the scale.

Figure 10. A set up of the polymer beads in the soil of a rain simulation.

Discussion

Liquid Polymer Solution Addition

Which polymer was used and the order of addition of the polymers had an effect on ammonia capture. A few of the methods of addition did not work well as either the polymers clumped, the solution didn't coagulate, or it just didn't capture the nutrients well. However, there were a few strategies that worked as the solution coagulated well enough to capture the nutrients, but produced material that is similar to the "cakes" from the original recipe. Alginate and pectin seem to work very well in capturing the ammonia and releasing it slowly. In terms of coagulants, 1010P works well but some dilutions seemed to work when added with the right polymers so additional tests to determine the correct ratio of coagulant to polymer would be very beneficial. Further research needs to be done in order minimize the amount of 1010P used.

Since the goal of this study is to not only create a slow-release fertilizer and be economically and environmentally safe, the need for larger amount of polymers and coagulants is not ideal. Thus efforts to minimize the amount of polymers and coagulants needed are warranted. Using the least amount of chemicals and products is best in this situation because the goal is to minimize costs and apply the least amount of chemicals on the field while achieving high level nutrient binding and slow-release in order to accomplish the goal of less nutrient runoff.

Nutrient Absorption with Polymer Beads

The beads are giving promising results. The fact that the beads absorb more ammonia when in raw manure is even more promising since that is what would be used anyway. More research is needed to determine why the absorption of dissolved ammonia is better from manure than from a pure ammonia solution, but these preliminary results seem promising. Next, the beads performance in soil should be tested with rain simulations, to determine the rate of ammonia released over time. If it is slow to release, which is the design these beads have anyway, then this is very promising for the future. Looking into the practicality of the beads is also important because this is eventually going to be big scale, agricultural field marketable so determining the feasibility of the beads is critical. Just exploring more about the beads could not only impact this research and design, but also other areas when photo-polymer beads could be utilized.

Rain Simulations

The rain simulations are designed to see how effective the mixture and cakes are at capturing and releasing the ammonia as it would when applied to a field. The results at this time, seem to indicate that pectin and alginate are more effective for capturing the ammonia than the cationic polymers. Conducting more rain simulations to repeat the results obtained is crucial in order to demonstrate reproducibility of this finding for ammonia capture and release. Plus, seeing many similar results can demonstrate if there is still any room for improvement, if there is any human error or error in general, make sure there aren't outliers that could skew the results and then utilizing all this information when implementing this in a bigger scale. A large scale pilot test will determine how well this treatment performs and would help determine any additional factors that must be controlled to optimize performance. Rain simulations provide an application based approach to this research as they can provide insight into what is working versus what is not and altering the recipe to optimize the potential the manure as a fertilizer can provide.

References

Becker, J.G., and R.E. Graves. 2004. Ammonia emissions and animal agriculture. In *Proceedings Mid-Atlantic Agricultural Ammonia Forum*. Woodstock, Va. March 16.

Costa, M., Shigaki, F., Alves, B., Kleinman, P., & Pereira, M. (2014). Swine manure application methods effects on ammonia volatilization, forage quality, and yield in the Pre-Amazon Region of Brazil. *Chilean Journal Of Agricultural Research, 74*(3), 311-318. doi:10.4067/S0718-58392014000300009

Dao, T. H., & Daniel, T. C. (2002). Particulate and dissolved phosphorus chemical separation and phosphorus release from treated dairy manure. *Journal Of Environmental Quality*, *31*(4), 1388-1398.

Gai, Z., Zhang, J., & Li, C. (2017). Effects of starter nitrogen fertilizer on soybean root activity, leaf photosynthesis and grain yield. *Plos ONE*, *12*(4), 1-15. doi:10.1371/journal.pone.0174841

Jokela, W.E, and J.J. Meisinger. (2008). Ammonia emissions from field applied manure: management for environmental and economic benefit. In Proc. Wisconsin Fertilizer, Aglime & Pest Management Conference. 47: 199-208.

Lugo-Ospina, A., Dao, T. H., Van Kessel, J. A., & Reeves, J. 3. (2005). Evaluation of quick tests for phosphorus determination in dairy manures. *Environmental Pollution (Barking, Essex: 1987)*, *135*(1), 155-162.

Mulbry, W., Westhead, E. K., Pizarro, C., & Sikora, L. (2005). Recycling of manure nutrients: use of algal biomass from dairy manure treatment as a slow release fertilizer. *Bioresource Technology*, *96*(4), 451-458.

Oun, A., Kumar, A., Harrigan, T., Angelakis, A., & Xagoraraki, I. (2014). Effects of Biosolids and Manure Application on Microbial Water Quality in Rural Areas in the US. *Water (20734441)*, *6*(12), 3701-3723. doi:10.3390/w6123701

Powell, J. M., & Rotz, C. A. (2015). Measures of Nitrogen Use Efficiency and Nitrogen Loss from Dairy Production Systems. *Journal of Environment Quality*, *44*(2), 336-344. doi:10.2134/jeq2014.07.0299

Saba, N., Awan, I. U., Baloch, M. S., Shah, I. H., Nadim, M. A., & Qadir, J. (2013). Improving Synthetic Fertilizer Use efficiency through Bio-Fertilizer Application in Rice. *Gomal University Journal Of Research*, *29*(2), 32-38.

Soils - Part 5: Nitrogen as a Nutrient. (n.d.). Retrieved December 06, 2017, from http://passel.unl.edu/pages/informationmodule.php?idinformationmodule=1130447042&topicorder=2&maxto=8

Van der Eerden, L.J.M., P.H.B. de Visser, and C.J. Van Dijk. 1998. Risk of damage to crops in the direct neighbourhood of ammonia sources. *Environmental Pollution* 102(S1): 49-53.