INORGANIC PHOSPHORUS FORMS AND EXTRACTABILITY IN ANAEROBICALLY DIGESTED DAIRY MANURE

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ABSTRACT. *On-farm anaerobic treatment is used for solids, odor and pathogen removal, and energy recovery. Research on anaerobic treatment of manure has focused on the influence of different process configurations and operational variables. Not much information is available on the effect of this treatment method on phosphorus (P) dynamics, which needs to be understood as manure nutrient management is a fundamental issue in agricultural non-point source pollution control. This study combines macroscopic experiments and chemical equilibrium modeling (Mineql+) to evaluate changes in P extractability and forms after anaerobic digestion of dairy manure. The objective of this study was to investigate the effect of different inoculum-to-substrate ratios (ISRs) on water extractable P (WEP) and the inorganic solid phases controlling P solubility. Dairy manure (substrate) and digested dairy manure (inoculum) were collected from an on-farm anaerobic digester. High ISR (HIS: ISR= 2.0) and low ISR (LIS: ISR= 0.3) samples were prepared on a volatile solids basis. These samples were subjected to mesophilic digestion in batch reactors without mixing for 120 d. A serial extraction method with extractant-to-manure ratios (EMRs) of 3-127 was used on the treated and untreated manure. Anaerobic treatment only decreased WEP from LIS extracts at EMR values of 3 and 7 by 28 % and 24 %, respectively. WEP in all other serial extracts of treated manure was higher regardless of ISR and EMR. Mineql+ simulations of the serial extraction data showed that struvite, beta-tricalcium phosphate (beta-TCP), and octacalcium phosphate (OCP) were the probable phases controlling P levels. Phosphorus solubility was controlled by struvite at lower EMRs (3-15) in the HIS extracts before and after anaerobic digestion. For the LIS system, struvite was in equilibrium with P for the same EMR range only after anaerobic digestion. An OCP- or beta-TCP-like phase controlled P solubility at higher EMR values.*

Keywords. *dairy manure, anaerobic digestion, phosphorus extractability, volatile solids destruction, serial and repeated extractions, inoculum-to-substrate ratios, calcium and magnesium phosphates.*

1. INTRODUCTION

Management of nutrients generated on animal farms has been receiving significant attention because of their oversupply, especially with phosphorus (P) on farm and near livestock housing. Physical and chemical treatment are being considered for on-site removal or immobilization of manure P. In addition to these technologies, anaerobic treatment of animal manure has been investigated due to the following potential benefits: (i) conversion of organic solids to biogas and renewable energy, (ii) mitigation of odor problems, and (iii) pathogen reduction (Zhang et al., 2000; Sung and Santha, 2003).

Phosphorus extractability and the dominant inorganic phases controlling its solubility in anaerobically digested animal manure have not been investigated in detail. First specific objective of this study is to determine changes in water extractability of P after anaerobic (mesophilic) digestion of dairy manure. Phosphorus availability is quantified in this study in terms of water-extractable P (WEP) using independent serial (i.e., mimicking single storm events) extraction method. Serial extraction refers to single-step extraction of the same sample batch with varying extractant-to-manure ratios (EMRs). The second objective is to elucidate the dominant inorganic P solid phases controlling its solubility using chemical equilibrium modeling with Mineql+ (Westall et al., 1976), a geochemical equilibrium software.

2. MATERIALS AND METHODS

Samples were collected from a dairy farm with a full-scale anaerobic treatment system in Markesan, WI. In this system, manure is collected using a flush system, conveyed to a mesophilic, mixed plug-flow anaerobic digester after screening, and finally digestate is subjected to solid separation using a screw press. The “substrate” sample was collected from the pit located before the screen. “Inoculum” was sampled from the effluent stream of the screw press. Batch anaerobic digestion was performed at two extreme inoculum-to-substrate ratios (ISRs), determined on a volatile solids (VS) basis, of 0.3 (low ISR; LIS) and 2.0 (high ISR; HIS). Serial extraction was used to extract P from anaerobically treated and untreated manures using 1-h extraction time. All analytical measurements were performed using the *Standard Methods* (APHA, 1995). Electrical conductivity, pH, dissolved calcium, dissolved magnesium, ammonium data of the serial extracts were combined with background concentrations of other manure components (e.g., sodium, potassium, chloride, volatile fatty acids, and bicarbonate). This data was used in detailed Mineql+ simulations to investigate probable P solid phases affecting P availability.

3. RESULTS AND DISCUSSION

a) Phosphorus Extraction:

Phosphorus extractability after anaerobic treatment is influenced by both the ISR and EMR values (Fig. 1 and 2). At the lowest EMR of 3, while P extractability by deionized water increased significantly (40%) after anaerobic digestion (Fig. 1) for the HIS system (Dissolved reactive P (DRP) concentration increased from 7.36 mg P L^{-1} to 10.34 mg P L^{-1}), the converse was true for the LIS system (Fig. 2). Anaerobic treatment decreased DRP concentration in the LIS extracts by 28 and 24 percent at EMR values of 3 and 7, respectively (Fig. 2). At EMR values between 15 and 127, a slight increase in P extractability occurred for the both the ISR values (5-15 % for the LIS system; 8-9 % for the HIS system).

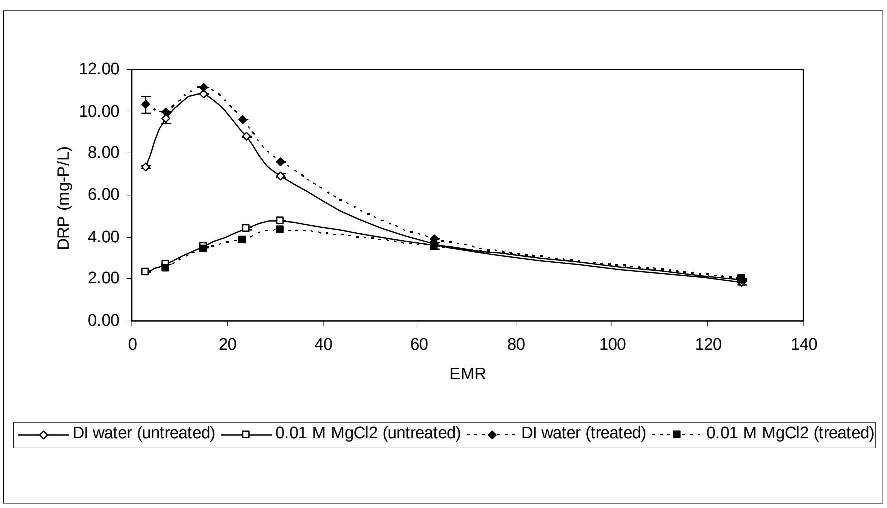

Figure 1. Dissolved reactive P (DRP) concentration in the high inoculum-to-substrate ratio (HIS) extracts as a function of extractant-to-manure ratio (EMR) for treated and untreated manure.

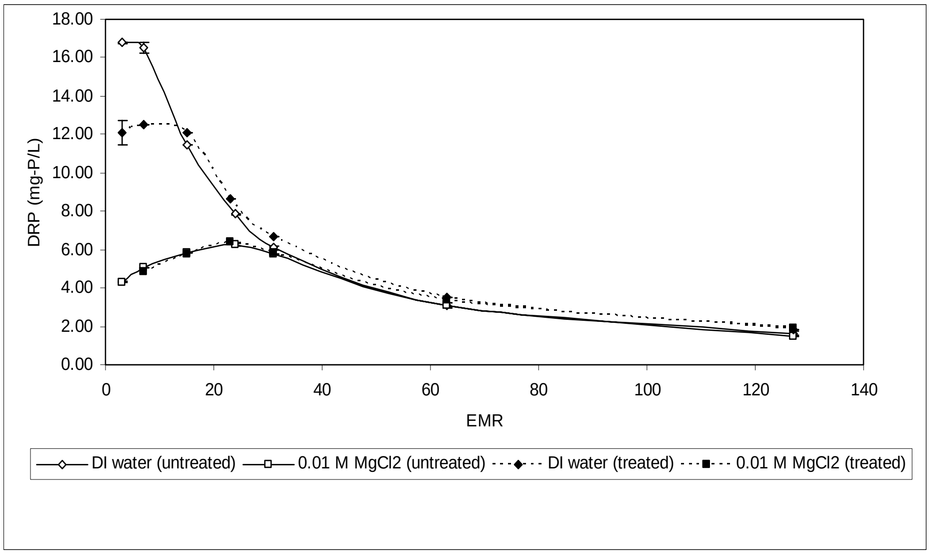

Figure 2. Dissolved reactive P (DRP) concentration in the low inoculum-to-substrate ratio (LIS) extracts as a function of extractant-to-manure ratio (EMR) for treated and untreated manure

Interestingly, DRP levels extracted by 0.01 mole L^{-1} $MgCl_2$ were not affected by anaerobic digestion and were significantly lower than those obtained in the DI water extracts up to an EMR of 63 and 31 for the HIS and LIS systems, respectively. Our hypothesis is that the presence of Mg in the extractant suppressed dissolution of P from an existing solubility-controlling Mg-P solid phase in the manure. At the highest EMR of 127, anaerobic treatment resulted in a slightly higher P extractability; average P extractability for the treated manure is 80 and 81% for the HIS and LIS systems, respectively, whereas the corresponding levels were 74 and 72% for the untreated manure.

b) Mineql+ Modeling:

Preliminary Mineql+ simulations showed that octacalcium phosphate (OCP), dicalcium phosphate dihydrate (DCPD), dicalcium phosphate anhydrous (DCPA), beta-tricalcium phosphate (β-TCP), and struvite were the probable P-containing solid phases in dairy manure. These phases were used in the detailed simulations (i.e., including important manure components in the background) to investigate the efficacy of probable solid phases to capture P release trends.

Measured DRP concentrations were in agreement with the concentrations dictated by struvite, OCP, and β-TCP phases, respectively, in ascending EMR order (data not shown). Struvite captured P release trend between EMR of 3 and 15 whereas an OCP/β-TCP-like phase appeared to determine DRP concentrations between EMR of 15 and 127 in HIS extracts. Anaerobic digestion did not have an impact on the probable phases and their stability ranges of the HIS extracts.

Although the probable phases controlling P solubility during serial extraction of the untreated LIS samples were the same as those determined for HIS, the effect of increasing amounts of the extractant (i.e., deionized water) was different. In undigested LIS extracts, P solubility controlling phase varied from OCP (EMR = 3) to OCP or struvite (EMR = 7) and β-TCP at the highest EMR (Fig. 3). After anaerobic treatment, DRP levels in equilibrium with struvite was in close agreement with measured DRP concentrations (3< EMR < 15) indicating it was more stable in the digested manure (Fig. 3 and 4).

4. CONCLUSIONS

Anaerobic digestion approximately increased dairy manure WEP by 15 percent at highest EMR. Effect of anaerobic digestion on the WEP was dependent on ISR at lowest EMR. Phosphorus solubility controlling phase shifted from more soluble Mg-P to sparingly-soluble Ca-P phases as the EMR increased. Struvite, OCP, and β-TCP determined P availability in similar EMR ranges of the untreated and treated HIS extracts. On the other hand, struvite controlled DRP over a wider range of EMR values (3-15) in the treated LIS extracts compared to the untreated samples. Dissolved reactive P was controlled by an OCP- or β-TCP-like phase at higher EMR (> 31) values in all serial extracts. Anaerobic treatment did not change the predominant P solid phases.

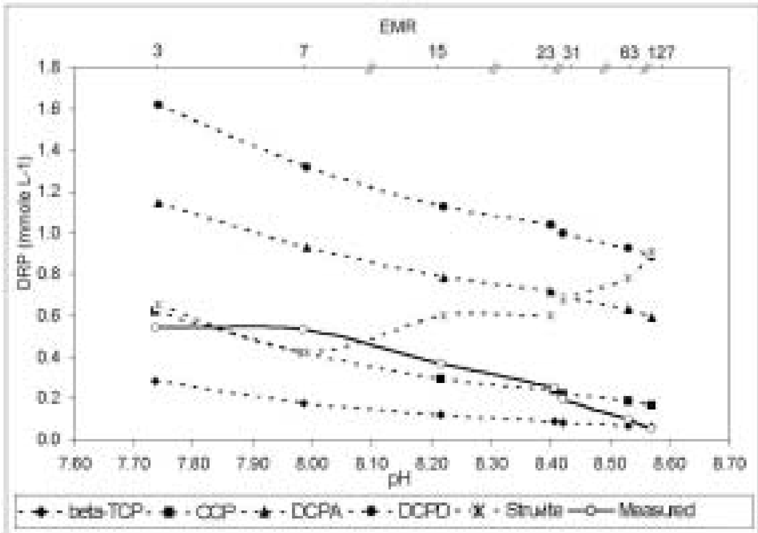

Figure 3. Simulated (equilibrium with various Ca phosphate phases and struvite) and measured DRP concentrations in LIS extracts before anaerobic digestion

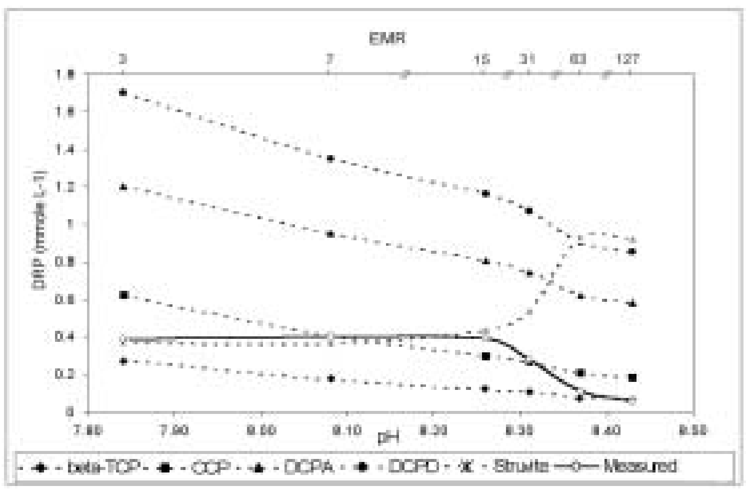

Figure 4. Simulated (equilibrium with various Ca phosphate phases and struvite) and measured DRP concentrations in LIS extracts after anaerobic digestion.

5. References

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