

## REMOVAL OF PHOSPHORUS FROM ANIMAL MANURES EXPERIENCES OF THE USDA - AGRICULTURAL RESEARCH SERVICE

### REMOÇÃO DE FÓSFORO DE DEJETOS DE ANIMAIS – EXPERIÊNCIA DO AGRICULTURAL RESEARCH SERVICE (ARS/USDA – EUA)

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#### 1. Abstract

A major problem in sustainability of animal production is surplus of manure phosphorus (P) exceeding land assimilative capacity. Land application of manure may result in P buildup in soil and increased potential for P losses through runoff and subsequent eutrophication of surface waters. A wastewater treatment process was developed for removal of P from livestock wastewater. Phosphorus is selectively precipitated using an alkaline earth metal after carbon and ammonia buffers are reduced with a nitrification pretreatment. The method was tested with wastewater collected from nine hog lagoons in North Carolina. In all cases, the soluble P was effectively recovered as P precipitate. When used as a lagoon retrofit, the technology enables precision control of the N:P ratio of the treated effluent to desired levels to match specific crop needs or to solve problems of P accumulation in soil or remediation of contaminated spray fields. The final product is calcium phosphate that can be exported from the farm and reused as fertilizer.

#### 2. Introduction

Swine waste disposal is a major concern often associated with large confined swine production. The liquid wastes generated in each production unit are generally treated in large anaerobic lagoons with intermittent disposal through land applications. This system was developed in the early and mid 20th century prior to the present trend toward fewer but larger operations concentrated within relatively small geographic areas. As a consequence, many counties in the U.S. Southern region produce more manure phosphorus (P) than available cropland can absorb (Barker and Zublena, 1994). This means that a considerable amount of manure P needs to be moved at least off farm and some needs to be transported longer distances further than county limits to solve distribution problems of this nutrient.

A key issue in sustainability of animal production is the imbalance between nitrogen (N) and P in the waste (Cochran et al., 2000; USEPA, 2001). Nutrients in manure are present in different proportion needed by

crops. For instance, the mean N:P ratio (4:1) in manure is generally lower than the mean N:P ratio (8:1) taken up by major grain and hay crops (USDA, 2001). Therefore, when manure is applied based on a crop's nitrogen requirement, there is a P buildup in soil and increased potential for P losses through runoff. Thus, P inputs accelerate eutrophication when it runs off into fresh water and has been identified as a major cause of impaired water quality (Heathwaite et al., 2000; Sharpley et al., 2000).

Methods used for P removal include flocculation and separation of solids using polymer addition and filtration or settling (Vanotti and Hunt, 1999). Although polymer treatment is effective for removal of organic P forms in liquid manure, it is not effective for removal of soluble P. This presents a problem in systems that use lagoons or other digestion or settling processes where most of the P in the liquid effluent is in the form of soluble phosphates. Past research efforts on P removal from animal wastewater using chemical precipitation have been frustrating due to the large chemical demand and limited value of by-products, such as alum sludge, or because of the large chemical demand and losses of ammonia nitrogen at the high pH required to precipitate phosphorus with calcium salts (Loehr et al., 1973; Westerman and Bicudo, 2000).

With the purpose of solving these problems, we have investigated and patented a process to remove soluble phosphorus from livestock wastewater (Vanotti et al., 2005). In this process, P is selectively precipitated using an alkaline earth metal after carbon and ammonia buffers are reduced with a nitrification pretreatment (Vanotti et al., 2003). This new process requires minimal chemical addition, reduces problems of ammonia emissions during separation of P from the aqueous phase, and recovers P in a reusable form. Our objective was to show that this new process removes P in a predictable way regardless of the source of swine wastewater. For this purpose, we used wastewater from nine swine lagoons that included most types of confined swine production in North Carolina.

### **3. Materials and methods**

Wastewater was collected from nine anaerobic swine lagoons in pork producing counties of North Carolina (Table 1). The sampled lagoons included most types of swine production facilities such as breeding, nursery, and finishing operations. Ammonia-N was the predominant form of nitrogen (> 95% of total N).

**Table 1.** Lagoon wastewater characteristics

Farm #	Operation Type	Location	TP	Soluble P mg/L	NH <sub>3</sub> -N
1	Nursery	Duplin Co.	60.9	34.4	296
2	Finishing	Duplin Co.	79.1	79.1	254
3	Finishing	Sampson Co.	61.0	44.7	1059
4	Finishing	Duplin Co.	85.2	77.7	1015
5	Finishing	Onslow Co.	26.0	17.8	402
6	Breeding	Onslow Co.	40.1	38.8	98
7	Finishing	Onslow Co.	65.4	64.3	251
8	Nursery	Onslow Co.	61.7	51.9	332
9	Research	Wake Co.	59.7	33.2	151

The treatment process consisted of a nitrification pre-treatment followed by addition of an alkali to the nitrified wastewater such as hydrated lime, which both increases the pH and precipitate P (Figure 1). Lagoon wastewater was treated in a nitrification vessel that contained nitrifying bacteria immobilized in pellets made of polyvinyl alcohol (PVA) polymer and an aerator that provided oxygen and fluidization of the immobilized pellets (Vanotti and Hunt, 2000). The nitrifying pellets increased microbial population in the vessel, which reduced total treatment time of nitrification (12-hour HRT); but other nitrification methods will provide satisfactory results (Szogi et al., 2004). During this nitrification pre-treatment, the natural carbonate alkalinity of the wastewater was exhausted in the process of ammonia oxidation. Aeration was stopped when > 90% of the natural alkalinity was consumed. For instance in farm #1, alkalinity decreased from 2292 mg CaCO<sub>3</sub>/L to 63 mg CaCO<sub>3</sub>/L in the process of ammonia oxidation to nitrate (approximately 300 mg N/L), and the pH decreased from 8.1 to 6.2.

The performance of the system using a pre-nitrification step (new process) was compared to applying the same amount of chemical to a lagoon liquid without using the pre-nitrification step (conventional process). Fixed amounts of hydrated lime [Ca(OH)<sub>2</sub>] were added to reaction vessels containing either wastewater nitrified or non-nitrified wastewater and mixed with a stirrer for one minute. Hydrated lime was added at a rate of 2, 4, 6, 8, 10, and 12 mmol Ca/L [1mmol Ca = 74.1 mg Ca(OH)<sub>2</sub>]. All experiments were duplicated. Treated wastewater was sampled in the supernatant after about a 0.5 hour gravity sedimentation period and analyzed for nutrients, pH and alkalinity according to Standard Methods (APHA, 1998).

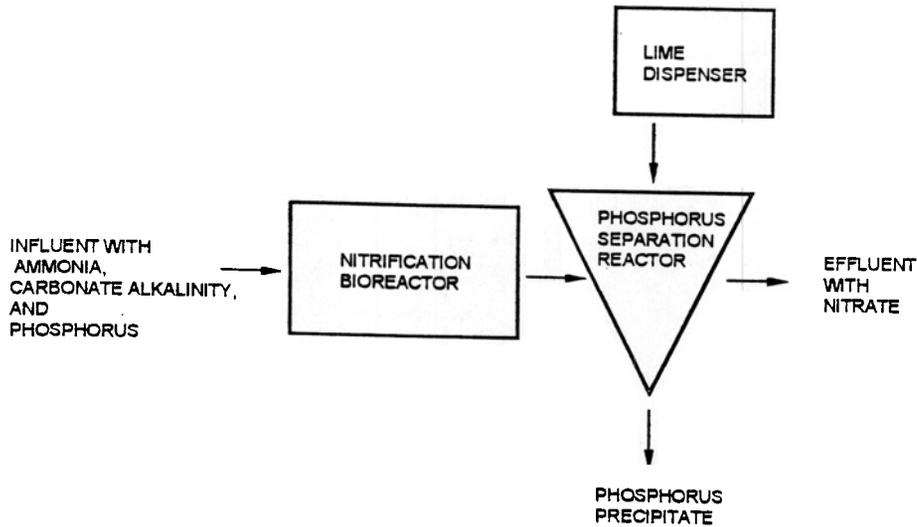


Fig.1. Schematic of the process for phosphorus removal from wastewater (Vanotti et al., 2005).

#### 4. Results

Phosphorus removal performance is summarized in Table 2 and Figure 2. Data shown in Table 2 indicates that the pre-nitrification step greatly improved P removal with lime application. Alkalinity and pH were much lower in pre-nitrified than in non-nitrified wastewater. With pre-nitrification, the pH of the wastewater is initially lowered with the acid produced by nitrifying bacteria even though a pH higher than 9 is needed to optimize precipitation of soluble phosphorus using Ca based compounds. Although the nitrified wastewater had to overcome a bigger pH deficit, it required less lime to do so because of the reduced alkalinity and buffer capacity. On average, > 90% P removal was obtained using pre-nitrification at Ca rates of 8 to 10 mmol/L (Figure 2). Average P removal in the non-nitrified treatment never exceeded 50% even at the highest Ca rate (12 mmol/L). In addition, since ammonia nitrogen has been converted to nitrate, increased pH by alkali addition does not result in gaseous  $\text{NH}_3\text{-N}$  loss (Vanotti et al., 2002).

By keeping the nitrate-N and removing variable amounts of P, the N:P ratio of the effluent can be adjusted to match the N:P ratio needed by crops. For example, using data from Edwards and Daniel (1992), a final N:P ratio of 10.7:1 and 13.4:1 would be needed to match wheat and coastal bermudagrass (*Cynodon dactylon*) specific nutrient uptake needs, respectively, which can usually be delivered with lower rates of Ca (2-4 mmol/L). Higher N:P ratios would be prescribed to remediate P-polluted sprayfields. This remediation process would use a negative mass phosphorus balance between

phosphorus applied and phosphorus removed by harvestable plant materials that is achieved with irrigation of treated wastewater having high N:P ratios. Wastewater treatment requiring high N:P ratios (300:1) (almost 100% removal of P) would be obtained with 8-10 mmol Ca/L. Figure 3 compares P removal of nitrified and non-nitrified wastewater to 100% removal when hydrated lime was added at a Ca rate of 10 mmol/L. The data indicate that the pre-nitrification step greatly reduced the amount of chemical needed for effective phosphorus removal and precipitation, and that the unique advantages of the system were significant to most confined animal operations.

In a previous study, chemical analysis indicated that calcium (Ca) and P were the predominant elements in the precipitate (Vanotti et al., 2003). The precipitate contained relatively small amounts of potassium (K), and magnesium (Mg), and no ammonia with a molar ratio of 1.0:2.7:0.1:0.2 for P:Ca:K:Mg. This elemental composition suggests that phosphates in calcium phosphate form are predominant in the final precipitate product.

**Table 2.** Removal of phosphorus from various North Carolina swine lagoons using hydrated lime with and without a nitrification pre-treatment.

Farm #	Initial Total P Concentration	Nitrification Pre-Treatment	pH Before Calcium <sup>1</sup> Addition	Alkalinity <sup>2</sup> Before Ca Addition	Calcium Application Rate (mmol/L)					
					2	4	6	8	10	12
	mg/L			mg/L	----- % P Removal -----					
	60.9	Yes	6.2	63	25	56	77	92	100	100
		No	8.1	2292	14	--	--	--	23	--
2	79.1	Yes	6.0	--	3	41	83	94	97	100
		No	8.6	--	11	14	43	51	56	78
3	61.0	Yes	6.4	130	36	76	80	100	100	100
		No	8.2	3477	1	3	7	16	24	17
4	85.2	Yes	6.2	78	22	61	89	99	100	100
		No	8.0	3062	1	9	14	13	20	19
5	26.0	Yes	6.4	156	61	86	93	100	100	100
		No	8.0	2858	27	41	55	77	83	89
6	40.1	Yes	7.5	129	69	69	86	94	100	100
		No	8.4	953	4	38	58	72	73	75
7	65.4	Yes	6.6	52	22	63	88	89	90	100
		No	7.9	1854	7	9	16	20	19	24
8	61.7	Yes	7.2	52	22	55	73	85	86	92
		No	8.5	2498	4	10	23	20	29	29
9	59.7	Yes	6.3	--	42	63	72	93	98	100
		No	7.9	--	27	44	57	67	68	66

<sup>1</sup> Calcium applied as Ca(OH)<sub>2</sub>; 1 mmol = 74.09 mg Ca(OH)<sub>2</sub>

<sup>2</sup> Alkalinity expressed as mg/L of CaCO<sub>3</sub>

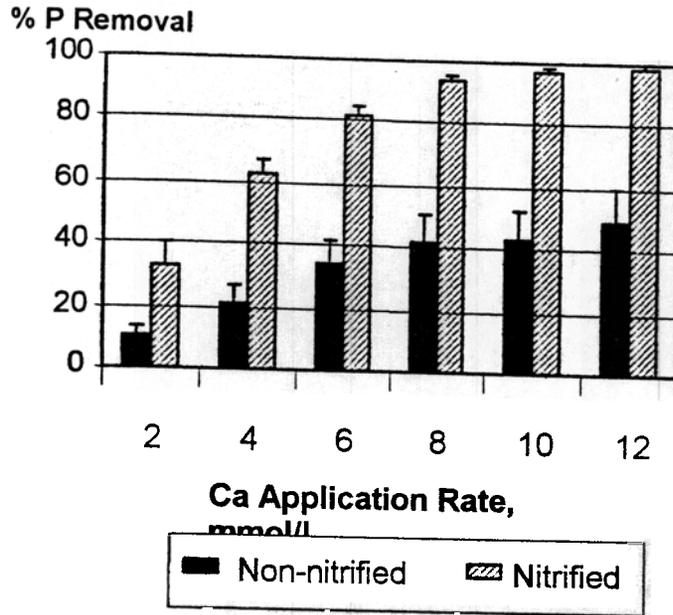


Fig. 2. Enhanced phosphorus removal from lagoon wastewater using hydrated lime and nitrification pre-treatment. Error bars are std. error of the mean, n=9 farms.

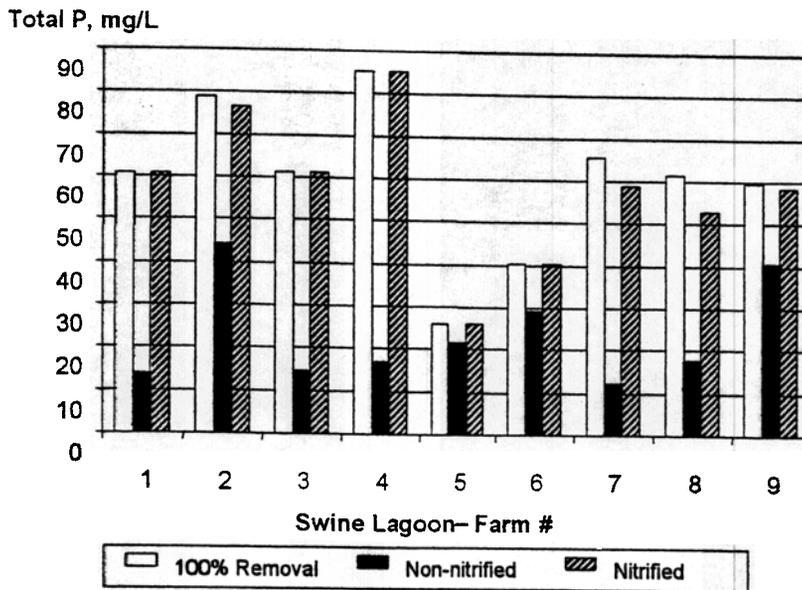


Fig. 3. Phosphorus removal from nine swine lagoons in North Carolina. Phosphorus was removed by adding hydrated lime (10 mmol Ca/L) to non-nitrified or nitrified lagoon wastewater. The 100% removal bar represents the initial total phosphorus content in wastewater.

## 5. Conclusion

A key issue in sustainability of animal production is the imbalance between N and P in the waste. Land application of manure based on N content results in P buildup in soil and increased potential for P losses through

runoff and ensuing eutrophication of surface waters. A wastewater treatment process was developed to solve this problem by removing soluble P from animal wastewater. Phosphorus is selectively precipitated using an alkaline earth metal after carbon and ammonia buffers are reduced with a nitrification pre-treatment. After testing lagoon wastewater from nine confined swine operations, our results show:

- The pre-nitrification step of wastewater greatly reduced the amount of chemical needed for the formation of calcium phosphate, and phosphorus precipitation and removal from wastewater were effective in samples from most confined animal operations.
- The amount of phosphorus removed, and consequently the N:P ratio of the effluent, can be adjusted in this process to match specific crop needs or remediate sprayfields.
- The final product is calcium phosphate that can be exported from the farm and reused as fertilizer.

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*Workshop on Technologies to Remove Nutrients  
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