Phosphorus Transformations in Swine Manure during Continuous and Intermittent Aeration Processes

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Abstract. *The work presented here was to determine the transformation of phosphorus (P) between different forms in the process of intermittent and continuous aeration. According to this study, aeration, at an airflow rate of 1.0 L/min, resulted in an increase in the manure pH of about one unit, from 6.5 to 7.5, within 24 hours, accompanied by a reduction in soluble ortho–P of 76%. This reduction in soluble P was apparently caused by the chemical precipitation that was indicated by a reduction in organic P and a simultaneous increase in insoluble inorganic P. The analysis of mass balances between the P fractions showed a large transformation of inorganic insoluble P into organic forms during the aeration period, which could overshadow the efficiency of soluble P removal by microbes. Because the manure contained about 73.5% insoluble inorganic P, it is suggested that solid–liquid separation should be performed prior to aeration to increase the efficiency of soluble P removal. In addition, continuous aeration did not show an advantage over intermittent aeration in terms of soluble P removal.*

Keywords. *Phosphorus fraction, Swine Manure, Aeration, Phosphorus Removal.*

Phosphate, especially soluble orthophosphate that is biologically available to algae (Sonzoghi et al., 1982), is generally considered to be the limiting nutrient responsible for eutrophication in surface waters. In recent years, public attention has been drawn to this problem, which is caused by agricultural runoff due to land application of animal manure. Reports have already shown that P runoff from crop fields receiving animal manure increases as the manure application rate increases (Westerman and Overcash, 1980; Mcleod and Hegg, 1984; Edwards and Daniel, 1993). Obviously, the P runoff is related to the excessive accumulation of P in the field. To ameliorate this situation, it is necessary to reduce the P level in manure to a level that both meets the needs of crops, based on their calculated phosphorus utilization efficiency, and reduces the potential of excessive P runoff.

Although chemical additives such as Fe, Al, and Ca have been employed to treat liquid manure and have proven to be efficient in removing nutrients, their high cost and secondary environmental pollution, by raising the Cl^- and SO_4^{2+} concentration and reducing the pH, limit their wide application. Biological removal of P, which has been used successfully in treating industrial and municipal wastewater, has therefore started to gain attention in treating agricultural wastewaters. This technique is based on the principle of an anaerobic process, believed to be a P release phase, followed by an aerobic process in which soluble P is converted into the biomass of microbes that can be removed by solids–liquid separation. The aerobic process is accomplished by aeration, which has been used in many places and has proven to be efficient in removal of BOD, COD, N, and P (Osada et al., 1991). It has been reported that about 60% to 90% of P can be removed by aeration, resulting in 30 to 50 mg/L P in the effluent (Have, 1980; Osada et al., 1991; Bicudo and Roberto, 1996).

Although much research has been done in using aeration to remove P from municipal and industrial wastewaters, little work has been reported on the utility of this technique in animal waste nutrient management. The reason may be that manure differs from municipal wastewater in its chemical compositions of phosphorus. Gerritse and Vriesema (1984) reported that manure contained substantial amounts of inorganic P, most of which is in insoluble forms. If this fraction of P is dissolved during the aeration process, the removal efficiency can be significantly reduced. It has also been reported that there are widely distributed groups of microbes that are able to convert insoluble inorganic P into soluble forms (Luo and Sun, 1993, 1994). During aeration, P in the inorganic insoluble forms may be released into solution as microbes remove soluble P from solution, hence decreasing the measured efficiency of P removal by the microbes. This may explain why high levels of P removal, as observed in treating non–agricultural wastewaters (soluble P < 1.0 or even < 0.3 mg/L) (Oldham, 1985; Arvin, 1985), have not been reported in treating agricultural wastewaters.

It should also be noted that in a biological treatment process, phosphorus is removed by incorporating it into cell tissue (Clark and Morriss, 1991). What happens in this process is the transformation of P from one form to another (e.g., from soluble form to organic form, which is biomass, or from insoluble form to soluble form, etc.), with the total P in the treated liquid unchanged. Because of this, the dynamic

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transformation of P among different forms during the treatment may provide useful information in developing new systems or in improving the performance of current designs. Unfortunately, this information is missing in the available literature. Without this information, development of practical, efficient aeration techniques for manure P removal may be hampered. Therefore, the objectives of this study are: 1) to determine the transformations of P fractions in swine manure during aeration, and 2) to reveal the mechanisms involved in the soluble P removal in swine manure by aeration.

Materials and Methods

Experimental Setup

The experiment was carried out in nine plastic columns, 91.6 cm in height and 15.3 cm in internal diameter. Each column was filled with liquid manure up to about 84 cm, leaving a headspace of 7.5 cm for stirring. Aeration was realized by an air pump (Catalog No. 13–875–220, Fisher Scientific Company, Hanover Park, Ill.), which provided air to each column at an airflow rate of 1 L/min, and was controlled by individual airflow meters mounted on the columns. The air was bubbling from the bottom of the column to maximize the travel distance and mixing effect. The intermittent aeration was accomplished by using a timer at 2–hour intervals (on/off). Three treatments with three replicates were studied, i.e., two aeration treatments (continuous vs. intermittent) and one control.

The manure used was collected from a finishing barn at the University of Minnesota Southern Research and Outreach Center. The manure properties are presented in table 1. During the test, the manure was sampled every 24 hours for the first 7 days and every 48 hours for the next 8 days. The length of the experiment was 15 days. At each sampling time, manure samples of 100 ml each were collected at a depth of 40 cm from the surface immediately after the manure in the columns was thoroughly agitated with a motorized paddle–stirrer for 5 minutes to ensure uniformity. The samples, after pH measurement, were stored at –20°C and were thawed before subsequent laboratory analyses.

pH Adjustment Experiment

In order to understand the role of raising pH alone in soluble P removal, 1.0 M of sodium hydroxide (NaOH) was added to eight raw manure samples at an increment of 1 ml to adjust the pH (table 2). The sample without the NaOH addition was used as control. The soluble ortho–P and pH were measured within 2 hours after the pH adjustment.

Table 1. Chemical properties of the test manure.

Property	Value
pH	6.47
N (%)	0.288
Total P (mg/L)	721.0
Soluble ortho–P (mg/L)	116.5
Organic P (mg/L)	74.2
Insoluble inorganic P (mg/L)	530.3
Organic carbon (%)	1.46
Total solids (g/L)	26.06
Total volatile solids (g/L)	20.69

Table 2. pH of samples from anaerobic treatment adjusted with 1.0 M NaOH.

pH	NaOH Added (ml)
6.464	0
6.698	1
7.046	2
7.550	3
8.170	4
8.538	5
8.743	6
8.880	7
8.929	8

Chemical Analysis

The pH of the manure samples was measured using a pH meter (CORION, Model 720A). Total P was measured after digestion with H_2SO_4–H_2O_2 and diluted to 100 ml (SSSA and ASA, 1996). Soluble ortho–P was determined in the filtrate after filtering 10–fold diluted manure using Whatman filter paper (Catalog No. 09–874–16c, Fisher Scientific Company). The measurement of total inorganic P was based on the method used in the determination of organic P in soil (SSSA and ASA, 1996). Insoluble inorganic P was expressed as the difference between total inorganic P and soluble ortho–P. Organic P was taken as the difference between total P and inorganic P. Ortho–P was determined colorimetrically as the phosphomolybdate complex after reduction with ascorbic acid (APHA, 1998). Nitrogen was measured using the Kjeldahl method. Organic carbon was measured by the tube digestion method recommended in the determination of soil organic carbon (SSSA and ASA, 1996). Total solids (TS) and total volatile solids (TVS) were determined using standard laboratory methods (APHA, 1998). For total solids determination, a well–mixed sample was evaporated in a pre–weighed dish and dried to constant weight in an oven at 105°C. The increase in weight over that of the empty dish represented the TS.

Results and Discussion

Chemical Composition of the Manure

As shown in table 1, the manure contained a considerable amount of inorganic insoluble P, which constituted the major part of total P (73.5%). Soluble ortho–P and organic P were found to be about 16.2% and 10.3% of the total P, respectively. The concentrations of these three P fractions are similar to those ranges reported by Gerritse and Vriesema (1984). As discussed early, because there are many groups of microbes widely present in soil that can convert insoluble inorganic P into soluble forms (Luo and Sun, 1993, 1994), the high proportion of insoluble inorganic P indicates a higher potential of P mobility in soils than for the organic P retained in microbes if the manure is applied to the cropland without phosphorus removal treatment. This may result in eutrophication as the excess P reaches surface water bodies.

Also from table 1, the manure contains only 74.2 mg/L of organic P but 14.6 g/L of organic carbon. The low concentration of organic P and relatively high concentration of organic carbon revealed that organic matter contains very little phosphorus. This observation may confirm the findings reported by Bicudo and Roberto (1996) that the organic residuals in manure were mainly composed of lignocellulosic materials, incorporated cellulose, and hemicellulose after digestion. These kind of organic materials are not able to retain P in solids, so the potential of P runoff may increase if the manure is applied to the cropland. Further research is needed to verify this.

SOLUBLE ORTHO–P

The mean variations in the soluble ortho–P in the three treatments are shown in figure 1. The soluble P was appreciably reduced by both the continuous and the intermittent aeration, with an average reduction of 64.0% for the former and 66.3% for the latter, and there was no substantial difference between the two treatments. Approximately, 75% of the soluble P removal was achieved within the first day for both aeration schemes, but further reduction was not observed in later days. This result suggests that the removal of P by aeration may be most effective in the first day of operation, and further aeration may not be needed in this regard.

pH CHANGE AND P REMOVAL

The most pronounced phenomenon of aeration is perhaps the pH rise in the manure (fig. 2). Aeration sharply increased the pH of the manure by approximately one unit within 24 hours, from 6.5 to 7.5, and slowly increased the pH to 8.5 thereafter. Little change in pH was observed in the non–aerated manure. Continuous aeration resulted in more pH increase than intermittent aeration. The drastic increase in pH brought about by aeration may be due to the conversion of ammonium into ammonia. This was documented by Stevens and Cornforth (1974), who found that passing a gas through slurry could increase pH up to 8 or 9 by purging the dissolved CO_2, which formed ammonium bicarbonate and kept the pH neutral. Enhanced breakdown of organic matter and hydrolysis of urea due to the introduction of O_2 into the manure can also increase the pH by increasing ammonia.

Figure 3 shows that, after being aerated for 24 hours, the samples with pH above 7.5 contained low levels of soluble P. This reduction in soluble P during the first day seems to be caused by the chemical precipitation resulting from the pH rise. It has been reported in previous work that raising pH could cause the precipitation of soluble ortho–P with metal ions such as Ca, Fe, and Al to form insoluble metal phosphates (Kox, 1981; Moore and Miller, 1994). A study by Campbell et al. (1997) revealed the nutrient status in swine manure at three depths in 8 farms and found that Ca concentration was almost as high as phosphorus, which provided evidence that this type of reaction can happen. Therefore, by this process, phosphorus could be transferred from soluble forms to insoluble inorganic forms.

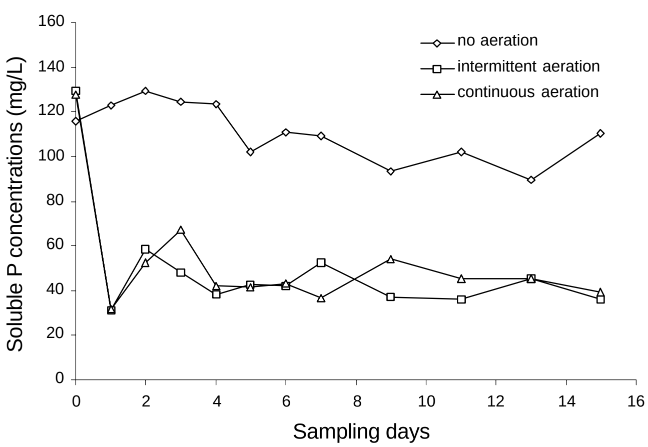

Figure 1. Fluctuations of soluble P concentrations in the manure for different treatments.

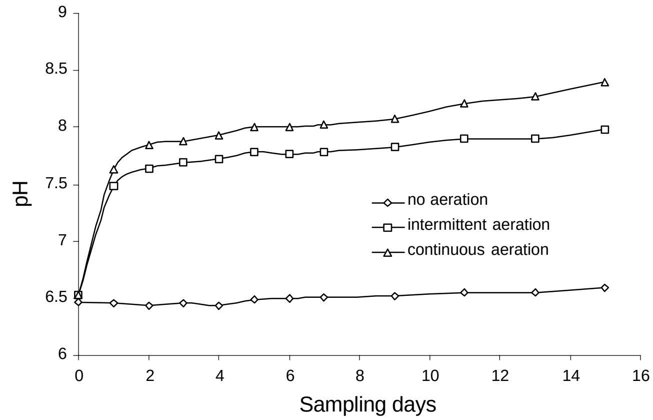

Figure 2. pH variations in the manure for different treatments.

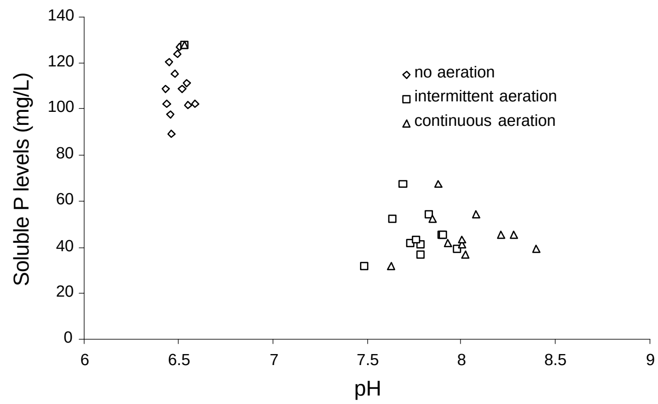

Figure 3. Relationship between soluble P concentrations and pH values in the manure for different treatments.

Figure 4 shows the reduction in soluble P achieved by adjusting the manure pH with 1.0 M NaOH without aeration. The soluble P was reduced from 120 mg/L to 70 mg/L (about 42% when the pH exceeded 7.5). This reduction is lower than that by aeration, implying that there may be other mechanisms of P removal involved in the latter case.

ORGANIC PHOSPHORUS

During the first day of aeration, a decrease in organic P was observed for both treatments, indicating a net organic P decomposition (fig. 5). A similar observation was reported by Stevens and Cornforth (1974), who found that the highest decomposition of organic matter was obtained in the first 2 to 3 days of aeration. In the following 2 days, the organic P showed a drastic increase and kept increasing slightly thereafter. Intermittent aeration showed a slower increase in organic P than continuous aeration, but the final organic P contents for both treatments were almost the same. As shown in figures 4 and 5, the increase in organic P (approximately 120 mg/L) was much larger than the amount of soluble P removed from the solution by the adjustment of pH alone.

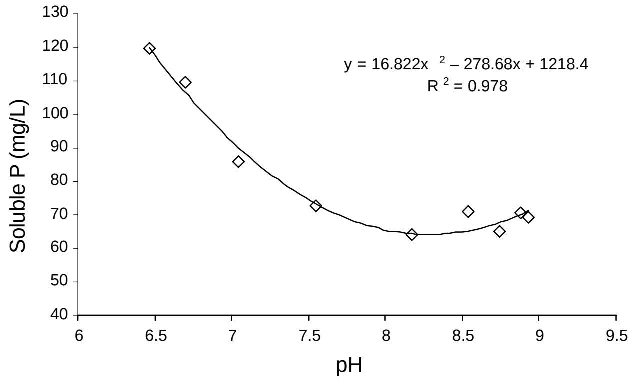

Figure 4. Relationship between soluble P content and pH adjusted with 1.0 M NaOH.

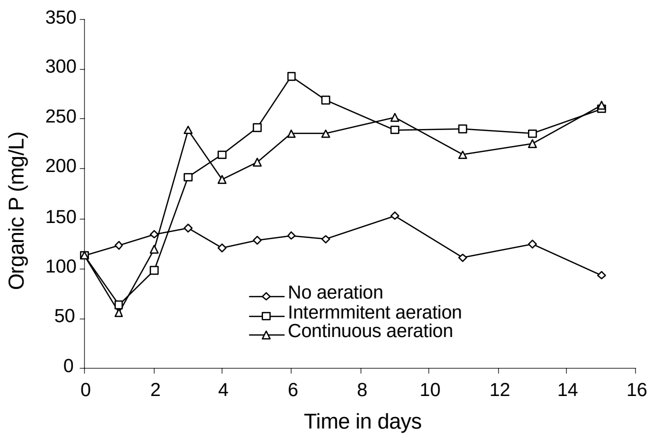

Figure 5. Organic phosphorus changes for different treatments during the experiment.

This indicated that more soluble inorganic P was transformed into the organic form by aeration. Considering that organic P is synthesized only by microbes, the biological uptake apparently occurred here in the manure during aeration, causing an increase in the organic P fraction, which substantially contributed to the soluble P removal in the liquid. From the above discussions, it may be concluded that microbes are able to remove more P than the pH adjustment.

Insoluble Inorganic P

A substantial increase in insoluble inorganic P in the first day of aeration was observed in both the intermittent and continuous aeration treatments (fig. 6). Because both the organic and soluble P were decreased in the first day, the increase of insoluble inorganic P should result from the chemical precipitation of the ortho–P under the raised pH. Therefore, it can be inferred that removal of soluble P by aeration in the first day was caused by the chemical precipitation process. In the following days, there were sharp decreases in the insoluble inorganic P, indicating the conversion of inorganic insoluble P into the organic fraction (fig. 5).

Balance of P Fractions

The mass balances of the three fractions of P for the three treatments are presented in figures 7 through 9. Figure 7

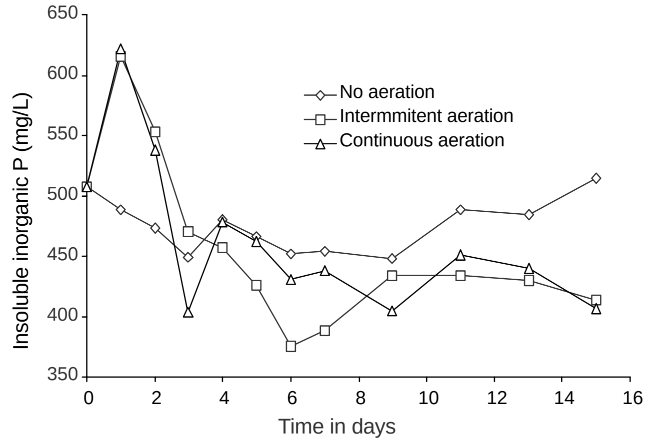

Figure 6. Changes in insoluble inorganic P for different treatments during the experiment.

shows that the three fractions of P in the treatment without aeration remained approximately at the same level during the entire period of experiment. Figure 7 also shows that the average level of organic P was relatively low (around 15%) but that of insoluble inorganic P was high (around 70%). Because the insoluble inorganic P is mainly contained in the manure solids, this observation verifies that separating solids from liquid may be the most efficient way to reduce the P content in the manure.

In both aeration treatments, an increase in inorganic insoluble P was observed in conjunction with decreases in both organic and soluble P in the first day of the test. After that, the organic portion increased appreciably, with almost no change in the soluble fraction. Apparently, the large increase in organic P originated from the decomposition of the insoluble inorganic portion. Considering that microbes cannot absorb insoluble P directly, a transformation process among different P forms may exist, as indicated in figure 10.

Luo and Sun (1993, 1994) reported that there are groups of microbes able to dissolve the insoluble inorganic P into soluble form through exudation of some chelators, such as organic acids. This process may have occurred during aeration in the manure in this study. The increase in the organic P did not necessarily lead to the removal of soluble P by the microbes due to the transformation of inorganic P into soluble forms. This may explain why no further reduction in soluble P was observed after the first day of aeration, although the microbes were continuing to accumulate soluble P from the solution (figs. 8 and 9). The decreased efficiency of soluble P removal after the first day may not be because of the inefficiency of the microbes but because of the conversion of inorganic P into soluble forms.

The above finding from this study has revealed an important scenario: the aeration process may not be able to further reduce soluble P concentration in liquid swine manure shortly after the initial stage unless the level of the insoluble inorganic P is greatly reduced. Because much of the insoluble inorganic P is contained in manure solids, separating solids from liquid to reduce the level of inorganic insoluble P should be suggested to improve P removal by biological processes.

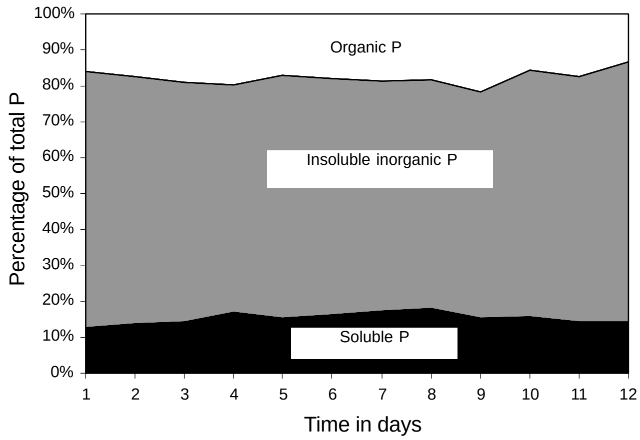

Figure 7. Phosphorus balance in the manure without aeration during the experiment.

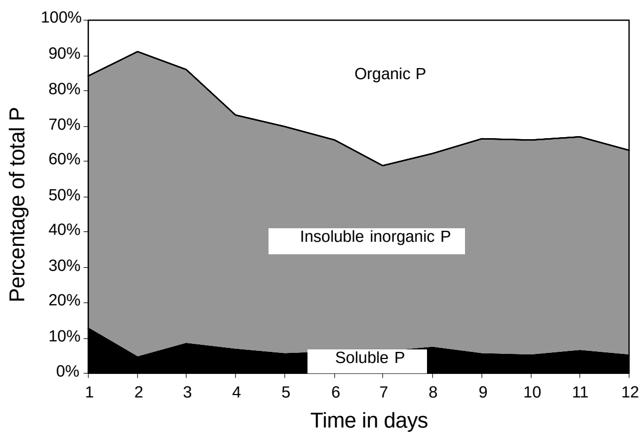

Figure 8. Phosphorus balance in the manure with intermittent aeration during the experiment.

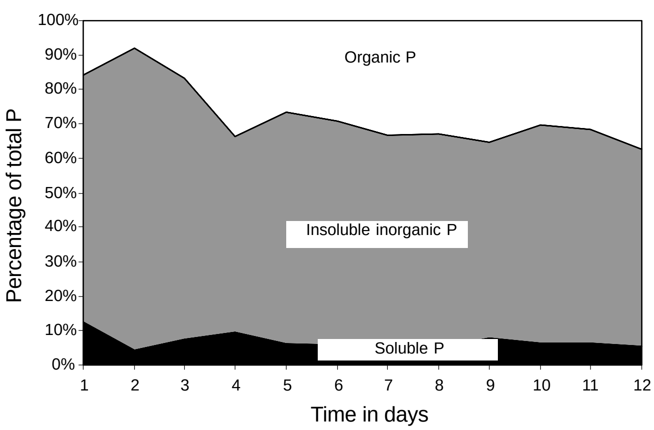

Figure 9. Phosphorus balance in the manure with continuous aeration during the experiment.

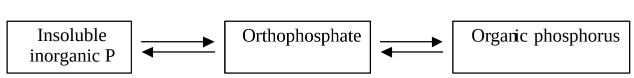

Figure 10. Diagram of potential transformation of P fractions during aeration.

Conclusions

1. Use of low–level aeration to raise manure pH without using NaOH showed that the manure pH increased by about 1 unit within the first day of operation for both the intermittent and continuous aeration treatments. In return, a reduction in the soluble P concentration by 76% was obtained. A sharp increase in inorganic insoluble P indicated that chemical precipitation played a major role in the soluble P removal. There was no difference between continuous and intermittent aeration in soluble P removal, suggesting that intermittent aeration may be a better option because it can potentially reduce energy consumption by 50% while still achieving the same level of P removal.
2. According to this study, fresh swine manure contained about 73.5% insoluble inorganic P, 10.3% organic P, and 16.2% soluble inorganic P. During the aeration treatment, the insoluble inorganic portion constituted the major P supply for bacterial growth. The mass conversion of the insoluble inorganic P into soluble forms, which ended up in the organic form in the biomass, virtually forfeited the merit of this treatment in reducing soluble P content in the liquid. Therefore, separating solids from liquid to reduce the level of insoluble inorganic P in the manure prior to aeration should improve the efficiency of soluble P uptake by the microbes.
3. Data from this study showed that microbial uptake is more efficient than pH adjustment in removing soluble P (a reduction of 120 mg/L vs. 50 mg/L). However, as seen in this study, aeration can also raise manure pH, thus leading to chemical precipitation of soluble P. Therefore, to moderately control the P content in manure to meet the actual needs of crops without excess energy consumption, more research is needed to study the possibility of developing feasible aeration systems that can be applied to current manure storage to provide minimum aeration for a short period of time solely for soluble P removal. Current manure handling practices should be reviewed and revised to accommodate the aeration system thus developed.

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