CHEMICALLY-ENHANCED GRAVITATIONAL SOLID-LIQUID SEPARATION FOR THE MANAGEMENT OF PHOSPHORUS IN LIQUID SWINE MANURE

BY

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ABSTRACT

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This laboratory column (125 cm high, 15 cm diameter) research investigated solids and P removal from liquid swine manure amended with calcium carbonate, magnesium sulphate, alum and polyacrylamide (PAM). Results showed that PAM was the most effective amendment for enhancing solids removal from manure containing 1% initial total solids (TS). The effectiveness of PAM was lower at 5% and 8% than at 1% due to resuspension of solids occurring at settling times beyond 4 h. After 24 h of settling, P removal from non-amended manure was comparable to that in amended manure and decreased with TS concentration for all amendments except alum, which was equally effective at all TS concentrations. These results indicate that, for manure containing 1% TS, P can be adequately removed by gravity separation without addition of chemical amendments while alum is a more effective amendment for removing P from manure containing higher (5% and 8%) TS.

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1. INTRODUCTION

1.1 Manure Production and Management Challenges

The swine industry has witnessed a significant growth over the years and plays a major role in the economy of Canada (CPC, 2009; Moyer et al., 2008; Salvano et al., 2006). This growth is due to the shift from the traditional method of raising pigs to confined feeding operations (CFO), which has increased swine production (Moyer et al., 2008). The increase in pig production has resulted in large quantities of swine manure generated annually (Choudhary et al., 1996; Moyer et al., 2008). Swine manure is a valuable source of nutrients, especially phosphorus (P) and nitrogen (N), to plants when utilized in an environmentally sustainable manner (Hodgkinson et al., 2002; Novak et al., 2000). Handling and disposal of the large volume of swine manure generated annually present a huge challenge to hog producers, not to mention the environmental issues associated with nutrient loss to water bodies following manure application on agricultural fields (Choudhary et al., 1996; Simard et al., 1995). Land application of swine manure is an established and environmentally acceptable method of utilizing manure (Choudhary et al., 1996). However, repeated application on the same piece of land in excess of crop P removal results in elevated soil test P concentrations, which may lead to P loss to the environment through surface runoff or leaching (Miller et al., 2011; Salvano et al., 2009; Sharpley et al., 2001).

Hog producers are under increasing pressure to comply with existing and emerging environmental regulations aimed at preventing excess nutrient loss into lakes and rivers, thereby protecting the water bodies from eutrophication (Allen and Mallarino, 2008 et al., 2008; Salvano et al., 2006; Slevinsky et al., 2009). A possible way of achieving compliance is by transporting excess nutrients in manure further afield from the vicinity of CFOs (Salvano et al., 2006). However, hauling liquid swine manure-borne nutrients for application on distant low-P cropland is uneconomical because of the large amount of water in the manure (Ndegwa et al., 2001; Rodriguez et al., 2005; Walker et al., 2010). Removing the nutrient-rich solids from liquid swine manure using manure treatment techniques, such as solid/liquid separation, provides the benefits of reducing the hauling cost and minimizing adverse effects of manure application on the environment (Fleming and MacAlphine, 2003; Masse et al., 2010; Walker and Kelley, 2003).

1.2 Solid-Liquid Separation: An Alternative Method

Solid-liquid separation has been employed in the treatment of drinking water and municipal wastewater for decades and offers potential for managing P in liquid swine manure (Walker and Kelly, 2003; Svarovsky, 2000). The technique involves the separation of solids from liquid manure using sedimentation (gravity settling), centrifugation, or filtration (using belt presses, screw presses, and screens). All these techniques have been proven to separate solids from manure slurries (Ford and Fleming, 2002; Hjorth et al., 2009; Møller et al., 2000). Ideally, the separated solid fraction is rich in nutrients, especially P, and can be economically hauled for application on P deficient soils, while the P-depleted liquid fraction can be irrigated onto fields near hog operations without elevating the soil test P (Vanotti et al., 2002; Rodriguez et al., 2005). Employing solid-liquid separation as a tool for manure treatment not only improves its handling properties, but also generates manure solids that can be utilized for either compost production or energy generation (Holmberg et al., 1983; Lo et al., 1993; Zhang and Westerman, 1997). Sedimentation is a preferred method used on most farms to remove solids from liquid manure when compared with other solid-liquid separation techniques (Ndegwa et al., 2001). The reason for this is that the cost of installing a sedimentation basin or tank is relatively low, and the system is simple to operate and can serve as a temporary storage for manure (Hjorth et al., 2009; Ndegwa et al., 2001).

Sedimentation is often carried out in sedimentation basins, settling tanks or ponds and its aim is to remove settleable solids from dilute liquid manure by gravitational settling either with (Nahm, 2005; Ndegwa et al., 2001; Zhu et al., 2004) or without the use of chemicals (Ndegwa et al., 2001; Power et al., 1995). Solids removal by sedimentation is based on the fact that suspended solids with densities greater than that of the water in which they are suspended tend to settle under the influence of gravity (Tchobanoglous et al., 2003; Wang et al., 2005). Large or coarse solids settle much faster than fine suspended solids that contain most of the P (Hjorth et al., 2009; Worley and Das, 2000; Zhang and Westerman, 1997). It takes a longer time for all the fine suspended solids in manure to settle by natural sedimentation. Hence, there has been growing interest in the potential of coagulants and flocculants to improve the removal of solids and nutrients by sedimentation (Barrow et al., 1997; Ndegwa et al., 2001; Power et al., 1995).

1.3 Chemically-Assisted Solid-Liquid Separation

Several studies have demonstrated that treatment of animal manure with coagulants and flocculants enhances solid-liquid separation (Christensen et al., 2009;

Hjorth and Christensen, 2008; Hjorth et al., 2008). The main goal of adding either coagulants or flocculants to manure is to promote the agglomeration of fine particles into large settleable flocs or aggregates that can be more easily removed from the liquid fraction (Sievers et al., 1994).

Commonly used chemical amendments are metallic salts, especially those of iron (Fe), calcium (Ca) or aluminum (Al), and/or synthetic organic polymers, such as polyacrylamide (PAM) formulations (Hjorth et al., 2009). Addition of coagulants [e.g., $FeCl_3$, $Fe_2(SO_4)_3$, $Al_2(SO_4)$, and $CaCO_3$] to manure results in coagulation of suspended particles by neutralizing the particles' negative surface charge and enhances P removal via precipitation of P by the cations constituting the coagulants (Powers and Flatow, 2002; Zhang and Lei, 1998). Polymers will flocculate particles and already existing flocs in manure by polymer bridging (Garcia et al., 2007; Vanotti and Hunt, 1999). Flocculation is generally influenced by the polymer's charge density and molecular weight (Masse et al., 2010).

Although there is information on gravity-assisted solid-liquid separation of swine manure as a P management strategy, very little information is available on solids and P removal from swine manure typical of hog operations in Manitoba. The results on solids and nutrient removal from studies conducted elsewhere may not be applicable to the manure generated in most hog barns in Manitoba because the composition of swine manure varies from one location to another and is largely influenced by feed rations, growth stage of pigs, manure collection methods and the quantity of water used in the manure collection system (Choudhary et al., 1996; Zhang and Westerman, 1997). A pilot study conducted by Slevinsky et al. (2009) to investigate the effectiveness of a settling tank to settle out solids and P by gravity separation from liquid swine manure collected from a hog barn in Manitoba showed that the extent of solids and P removal was reduced at high TS (6.6%). Although results from the study demonstrated the potential of gravity separation as an option for managing manure solids and P, no firm conclusions could be made from the study because of inadequate replication of treatments. Given this background, the overall objective of this thesis research was to determine the effects of calcium carbonate ($CaCO_3$), magnesium sulphate ($MgSO_4$), aluminum sulphate (alum) and Superfloc C494 (PAM) on the removal of solids (Chapter 2) and nutrients (particularly P and N) (Chapter 3) from liquid swine manure of varying solids concentrations.

Chapter 2 of this thesis provides information on solids removal from liquid swine manure amended with $CaCO_3$, $MgSO_4$, alum and PAM vs. non-amended manure (control). Amendment effects are reported for different swine manure initial solids concentrations. Chapter 3 provides results on nutrient removal from swine manure of varying solids concentrations amended with the four chemicals vs. non-amended manure.

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2. GRAVITATIONAL SETTLING OF SUSPENDED SOLIDS IN LIQUID SWINE MANURE: EFFECTS OF MANURE SOLIDS CONCENTRATION AND CHEMICAL AMENDMENT APPLICATION

2.1 Abstract

There is growing interest in the gravity-assisted solid-liquid separation of swine manure as a phosphorus (P) management strategy for manure on hog operations. The P-rich and usually nitrogen- (N-) depleted solid fraction is more economical to haul to areas of low fertility, thus obviating application of manure on high-P soils commonly found in the vicinity of hog operations. This in turn ensures that adverse environmental impacts associated with land application of swine manure on P-rich soils are minimized. This study investigated the effectiveness of four chemical amendments [calcium carbonate ($CaCO_3$), magnesium sulfate ($MgSO_4$), aluminum sulfate (alum) and Superfloc C494 (PAM)] at enhancing gravity-assisted solid-liquid separation of swine manure slurries containing 1%, 5%, and 8% total solids. Manure treated with the chemical amendments was placed in 21-L settling columns (15 cm diam. and 120 cm high) and allowed to settle. Samples collected from the 30-, 60-, and 90-cm depths (representing the 15- to 45-, 45- to 75, and 75- to 105 cm depth intervals or layers) after 0.5, 1, 2, 4, 8, and 24 h of settling were characterized for total solids concentration (TS). In manure containing 1% TS, PAM was the most effective at enhancing solids removal within the first 4 h of setting. For both the 15- to 45- and 45- to 75-cm layer, averaged across sampling times, solids removal was highest with PAM (mean 47%), compared with alum (mean 22%), $MgSO_4$ (mean 20%) and the control (mean 21%) in manure containing 1% initial TS. Solids removal

from $CaCO_3$-amended manure did not differ significantly from that in PAM-treated manure. There was also evidence of solids removal at the 90-cm depth in manure containing 1% initial TS, with removal decreasing in the order PAM (49%) > $CaCO_3$ (35%) > control (26%) > $MgSO_4$ (18%) > alum (11%). Solids removal from the 15- to 45-cm layer in PAM- and alum-amended manure, averaged across sampling times, decreased as the initial TS increased from 1% to 8% TS. Settling times greater than 4 h in PAM-treated manure containing 5 and 8% TS resulted in re-suspension of the separated solids to the 0- to 45-cm layer. Solids removals from the 45- to 75-cm layer in manure containing both 5% and 8% initial TS was significantly greater in manure treated with $CaCO_3$ and in the control compared with manure treated with alum and PAM. Across initial TS concentrations, $CaCO_3$ resulted in greater removal of solids from both settling depths compared with $MgSO_4$, which was the least effective amendment.

Overall, PAM was the most effective amendment for enhancing solids removal from liquid swine manure. However, resuspension of settled solids after 4 h of settling in manure containing 5 and 8% TS suggests that PAM may not be a suitable amendment for high-TS liquid manure, unless the solids-liquid separation system can be designed to pump out the liquid fraction or remove the settled solids within 4 h.

2.2 Introduction

Manure management and disposal are major challenges for swine producers in Manitoba due to the high phosphorus (P) concentration in swine manure, which presents a risk of eutrophication of surface water bodies (Choudhary et al., 1996; Flaten et al., 2007; Zhu et al., 2004). Repeated application of manure on the same piece of land in excess of crop P removal results in elevated soil test P concentrations, which may lead to P loss to the environment through surface runoff or leaching (Miller et al., 2011; Salvano et al., 2009; Sharpley et al., 2001). Liquid swine manure in most hog barns is generally dilute (i.e., low in solids) due to the large volume of water used to flush the waste from pens, and is characterized by fine suspended solids that contain most of the organic nutrients, especially P and N (Gao et al., 1993; Masse et al., 2005). In some jurisdictions, such as Manitoba, hog producers may have to transport excess nutrients in manure further afield in order to meet stricter environmental regulations aimed at preventing excess nutrient transport into lakes and rivers following land application of swine manure (Slevinsky et al., 2009). However, hauling liquid swine manure to distant fields is uneconomical because of the large volume of water in the manure (Ndegwa et al., 2001; Vanotti et al., 2002; Walker et al., 2010). Separating the manure into solid and liquid fractions provides the benefits of reducing the hauling cost and minimizing adverse effects of manure application on the environment (Beline et al., 2004; Masse et al., 2010; Walker and Kelley, 2003). The separated solid fraction is rich in P and other nutrients and can be more economically hauled for application on P deficient soils, while the P-depleted liquid fraction can be irrigated on fields near hog operations without elevating the soil test P levels (Vanotti et al., 2002; Rodriguez et al., 2005).

Sedimentation (gravity settling) is one of the many solid-liquid separation techniques, which have been used to remove solids from dilute swine manure (Ndegwa et al., 2001; Power and Flatow, 2002; Zhu et al., 2004). Suspended solids with densities greater than that of the water in which they are suspended tend to settle under the influence of gravity (Wang et al., 2005). Large or coarse solids settle much faster than fine suspended solids that contain most of the P (Hjorth et al., 2009; Wang et al., 2005; Zhang and Westerman, 1997). In contrast, fine suspended solids contained in liquid swine manure take much longer to settle by natural sedimentation. However, agglomeration of the fine particles into flocs or aggregates can enhance their sedimentation (Rodriguez et al., 2005; Power and Flatow, 2002; Vanotti and Hunt 1999).

Several studies have demonstrated that treatment of liquid swine manure with coagulants and flocculants can enhance solid-liquid separation (Hjorth and Christensen, 2008; Worley and Das, 2000; Zhu et al., 2004). However, it is very difficult to make generalized comparisons because of the different procedures used in the studies. In the majority of sedimentation studies, the effectiveness of chemical amendments was evaluated in 1-L jar tests or Imhoff cones used for standard settleable solids tests (Power and Flatow, 2002; Vanotti and Hunt, 1999; Zhu et al., 2004). Additionally, nearly all tests were performed using manure with low solids concentration (TS <1%), with amendment performance assessed at the end of the settling period rather than at different time intervals.

Other studies (Ndegwa et al., 2001; Zhang and Lei, 1998) did utilize the method suggested by Tchobanoglous et al. (2003) to determine the settling characteristics of suspensions of flocculated particles. This method involves the use of settling columns of similar height to settling tanks that would be used on hog operations. The use of settling columns more closely mimics practical situations when compared with settling jar tests (Imhoff cones) used in many previous studies. Ndegwa et al. (2001) used 91-cm columns, 15 cm in diameter, which resembled actual sedimentation pits/tanks in height. Ndegwa et al. (2001) reported that aluminum sulfate and ferric chloride addition at 1500 mg L^{-1} enhanced solids removal from swine manure containing 1% initial TS by 96% and 66-76%, respectively. The experiment conducted by Zhang and Lei (1998), is one other study that has examined settling of swine manure with different initial TS (0.5, 1.0, 1.5, and 2.0%) following coagulation in more relevant columns (12.7 cm diam. and 100 cm high) compared to settling jars test. They reported that the settling rate of the suspended solids decreased as the manure initial TS increased. Also, a greater amendment dosage was required for higher manure initial TS.

The overall objective of this study was to evaluate the effectiveness of chemical amendments ($CaCO_3$, $MgSO_4$, alum and PAM) in enhancing settling of solids from liquid swine manure of varying initial total solids content. The specific hypotheses were: (i) solids removal in chemically-treated manure will be greater than in non-amended manure, and (ii) the quantity of solids removed will decrease with increasing initial TS concentration of manure.

2.3 Materials and Methods

2.3.1 Settling Columns

Five settling columns were assembled using 125-cm high, 15-cm diam., 0.6-cm thick cast acrylic tubes. The height of the columns was selected to closely match that of a typical on-farm settling tank (Tchobanoglous et al., 2003). The bottom of each column was sealed with flat acrylic glass using glue. Holes (1.2 cm diam.) were drilled at the 35-, 65- and 95- cm depths (measured from the top of the column) and fitted with valves (assembled using PVC nipples, micro valves, and caps) to enable manure sample collection at these depths (Fig 2.1), corresponding to depths of 30, 60, and 90 cm below the surface of the manure column.

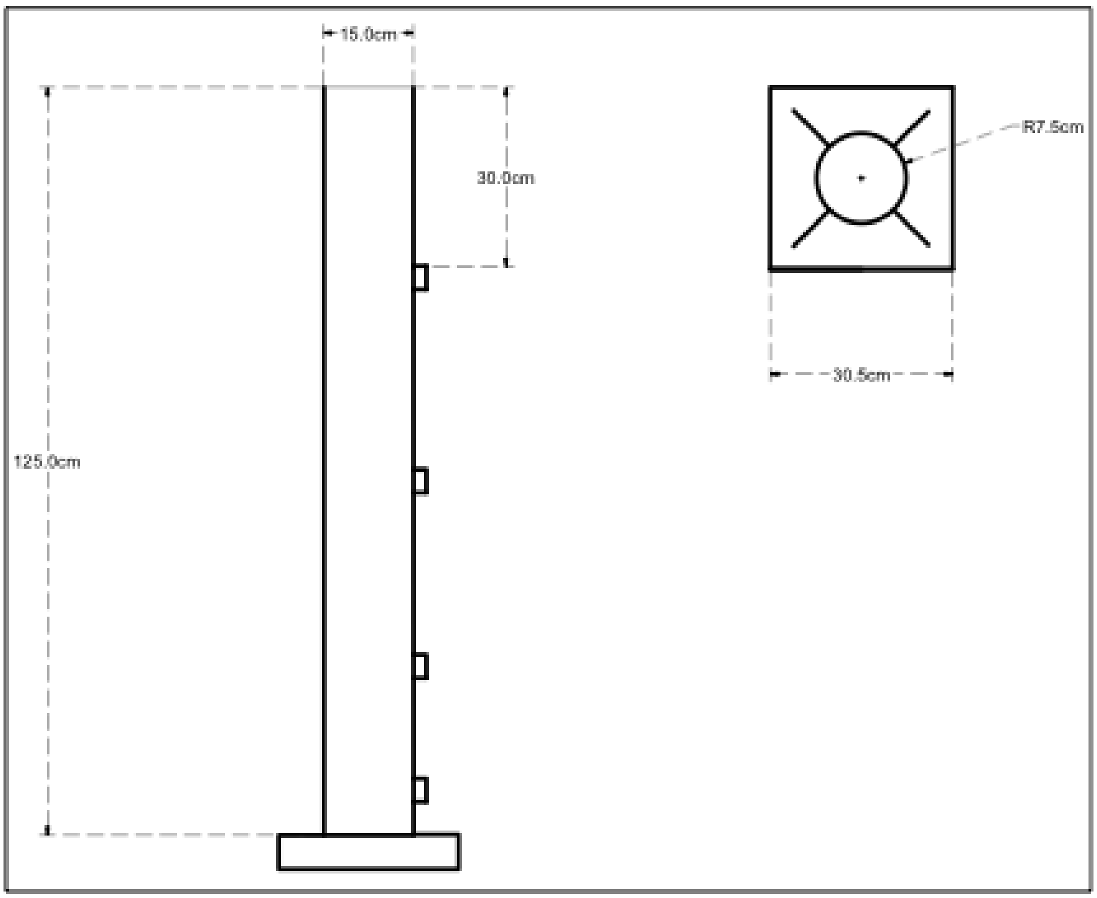

Figure 2.1 Schematic of the settling column used in the gravitational solid-liquid separation of liquid swine manure.

2.3.2 Manure Collection

Swine manure used in the sedimentation experiment was collected from a commercial swine operation near Niverville, MB. The operation has a capacity of approximately 4000 pigs, which are raised from weaning until they are ready for the market. Pig diets are supplemented with phytase to ensure better utilization of phytate-P, which is the main form of P in grain diets (Daumer et al., 2004). Addition of phytase to animal feed also obviates the need for inorganic P supplementation and is environmentally desirable because of the reduced P excretion in the feces (Sommer et al., 2008). Liquid manure collection at the swine operation involves an under-slat flushing system. In this system, manure is washed with fresh water through the slat into pits underneath the back of each pen using sprinklers that are on a timer system. The pits are emptied when full at least once a week, with manure draining from the pits to the lift station, from which it is pumped out to the lagoon.

The first manure batch, with a solids content of about 3%, was collected directly into twenty, 20-L plastic containers from an effluent pipe discharging into the lift station on a concrete floor. The second batch was collected by scraping from the pen floor just before the manure was flushed into the pits. This batch was meant to provide manure with higher solids concentration (>3%). Samples from the two batches were analyzed for total solids (TS) concentration according to APHA et al. (2005) procedures. The initial TS concentration (dry wt. basis) of the second batch was 17%. Manure from the first batch was diluted with fresh water to attain a TS concentration of 1% while the second batch was similarly diluted to TS concentrations of 5% and 8%. Manure was stored at 4℃ to prevent digestion and bacterial decomposition of solids and organic nutrients prior to the sedimentation experiment (Vanotti and Hunt, 1999; Zhu et al., 2000).

2.3.3 Sedimentation Experiment

The experiment was laid out in a randomized complete block design with three replications. The treatment layout was a split plot with solids concentration as the whole plot and amendment as the subplot. A control treatment consisting of non-amended manure was included for comparison. Amendment rates were based on results from a preliminary experiment using manure containing 1% initial TS concentration. Three coagulants (aluminum sulphate hydrate [alum, $Al_2(SO_4)_3.13H_2O$], calcium carbonate ($CaCO_3$), and magnesium sulphate ($MgSO_4$)) and a flocculant (PAM) were added to liquid swine manure of varying initial TS concentration to evaluate their effects on solids removal. The polymer (Superfloc C-494, Kemira Water Solutions, Inc., Lakeland, FL) was a moderately charged (19 mole % charge density), high-molecular weight, cationic polyacrylamide (PAM) powder with ~93% active polymer. Superfloc C-494 is a copolymer of acrylamide and methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate (Garcia et al., 2007; Vanotti and Hunt, 1999).

In the preliminary experiment, liquid manure (3% TS) was diluted with fresh water to a solids concentration of approximately 1%. Portions of the diluted manure were then treated with alum, $CaCO_3$, $MgSO_4$ and PAM at rates (Table 2.1) based on previous studies (Power et al., 2002; Vanotti and Hunt, 1999; Zhang et al., 1998). Immediately after mixing-in the chemicals (time 0), manure samples were collected into 50-mL centrifuge tubes while the rest of the liquid was carefully poured into settling columns.

The settling columns were filled such that manure slurry was 5 cm below the top of the column, with the result that the sampling holes were 30, 60 and 90 cm below the initial slurry level. Five columns were run at a time, four of which contained manure treated with chemical amendments while the fifth contained non-amended (control) manure. This setup was replicated three times.

Fifty-milliliter samples were taken after 0.5, 1, 2, 4, 8 and 24 h from the 30-, 60- and 90-cm depths using the valves described above. The thickness of the settled solids layer was measured at each sampling time while the head drop of the manure in each column was recorded at the end of each run. After 24 h, the liquid portion was siphoned out of the column and the solids mass at the bottom of the settling column weighed. Solids removal from the manure above each sampling depth was calculated by subtracting the solids content at each sampling time from the solids content measured at the start of each run (i.e., at time 0).

Sample pH and electrical conductivity (EC) were measured using a digital pH/conductivity meter (Accumet AP85, Fisher Scientific, Singapore). Total suspended solids concentration was determined using standard methods (APHA et al., 2005). Briefly, 15-mL aliquots of manure were measured into aluminum foil and placed in the oven at 105°C for 24 h. The oven-dry weight represents the amount of solids that remained in the liquid manure at the respective sampling depth after gravity settling for a given sampling period. Approximately 35 mL of the manure was stored in a freezer at -19°C until analysis for total P, total Kjeldahl N (TKN), ammonium-N (NH_4-N), potassium (K), calcium (Ca), and magnesium (Mg) concentrations.

Results from the preliminary experiment indicated that there were no significant differences in solids removal among amendment rates tested using manure containing 1% initial TS concentration (Table 2.1). Therefore, the lowest amendment rate tested for each amendment was used to determine amendment rates for manure containing 5% and 8% initial TS concentrations (Table 2.2)

Table 2.1 Amendment rates tested in liquid swine manure containing 1% initial total solids concentration.

Rate Level	**Amendment application dosage (mg L^{-1})†**			
	$CaCO_3$	**$MgSO_4$**	**Alum**	**PAM**
Low	2856	3256	549	122
Medium	4070	4884	823	183
High	8140	9768	1646	366

† Concentration of amendments in swine manure in the 21-L settling column.

Table 2.2 Dosage of chemical amendments in liquid swine manure of varying solids content.

Total solids conc. (%)	**Amendment application dosage (mg L^{-1})†**			
	$CaCO_3$	**$MgSO_4$**	**Alum**	**PAM**
1	2856	3256	549	122
5	14548	16801	3999	636
8	21038	25245	6083	946

† Concentrations of amendments in swine manure in the 21-L settling column.

2.3.4 Calculations

Solids removal was calculated as follows:

$$\text{TS removal (\%)} = [1- (TS_t / TS_0)] \times 100$$

where TS_t is the mass (g) of TS settled out of a given volume at time t and TS_0 is the mass of TS (g) in the same volume before settling commenced (time t_0) (Power and Flatow, 2002).

For manure containing 1% initial TS, the drawout was fixed at the 60-cm depth and the TS removal was calculated at this depth. For comparisons including PAM at the 5 and 8% initial TS concentrations, the drawout was fixed at the 30-cm depth because of clogging of the sampling ports at the 90-cm depth and the resuspension occurring in columns treated with PAM. As expected, solids that settled out of the upper layers were deposited in the layers below. Hence, net accumulation will be the term used in this chapter to describe cases where calculated solids removal below the 30-cm depth was negative.

2.3.5 Statistical Analysis

Net solids removal calculated for each depth at different sampling times were assessed using the MIXED procedure for repeated measures in SAS (SAS Institute, 2008) with sampling time as the repeated factor. Initial solids concentration, amendment, sampling time and sampling depth were fixed effects in the mixed model while replications and their interactions with fixed effects were random effects. The spatial power [SP(POW)] covariance structure was used in the model in which the repeated factor (sampling time) had variable intervals. Treatment differences were considered significant if $P < 0.1$ using the Tukey method.

Results for solids removal (net solids removal) by PAM in manure containing 5 and 8% initial TS concentration beyond 4 h settling time were not included due to the re-suspension of the flocculated solids to the surface above the 45- to 75-cm depth of the column observed during the sedimentation experiment. This re-suspension was likely due to biological activity releasing gas bubbles, which resulted in the floatation of the separated flocs (Martinez et al., 1995; Vanotti and Hunt, 1996). Therefore, results for solids removal are presented for three scenarios: (i) for the 1% initial TS concentration, all sampling times and two depths (30 and 60 cm) were assessed; (ii) also for the 1% initial TS, the 90 cm depth was analyzed separately to represent the ideal drawout and also because three depth levels could not be analyzed as the second of two repeated measures since time (first repeated factor) intervals were unequal; and (iii) for the 5 and 8% initial TS, settling was assessed for the first 4 h of sedimentation to avoid data distortions resulting from solids resuspension in PAM treatments. Net solids removal is described herein as solids removal if positive or net accumulation if negative.

2.4 Results

2.4.1 Net Solids Removal at the 30- and 60-cm Depths at 1% Initial Total Solids Concentration

Amendment × time ($P = 0.01$) and amendment × depth ($P = 0.02$) interactions were significant for solids removal in manure containing 1% initial TS (Table 2.3). However, the Tukey test was not powerful enough to detect any differences in pairwise comparisons. Main effect differences are therefore discussed in this section.

2.4.1.1 Amendment Effects

PAM was the most effective amendment and significantly improved solids removal by 62% (i.e., from 29% to 47%) compared to the control. Alum (27%), $CaCO_3$ (38%) and $MgSO_4$ (20%) did not significantly affect solids removal relative to the control (29%).

2.4.1.2 Settling Time Effects

Within the 24-h sampling period and averaged across amendments and depths, solids removal increased as a quadratic function of settling time (solids removal = $29.5 + 0.88x - 0.02x^2$, where x is settling time, $r^2 = 0.88$, $P = 0.04$). After 4 h of settling, however, the solids removal was minimal.

2.4.2 Net Solids Removal at the 30- and 60-cm Sampling Depths during the first 4 h of Sampling

There were significant amendment × initial TS × time ($P = 0.02$) and amendment × initial TS × depth ($P = 0.03$) interactions for solids removal (Table 2.3). In manure containing 1% initial TS, PAM resulted in significantly greater solids removal relative to $MgSO_4$, alum and the control at all sampling times and averaged over the 30- and 60-cm sampling depths (Fig 2.2a). Calcium carbonate resulted in the second highest solids removal, which, however, was not significantly different from the other four treatments, with the exception of the control at the 2-h sampling time, which showed an inexplicable decrease in solids removal compared to the preceding sampling times. After 4 h of settling, solids removals in PAM- (47%) and $CaCO_3$-treated (41%) manure were significantly greater than in $MgSO_4$-treated manure (21%) but similar to the control (29%) and alum-treated manure (25%).

In manure containing 5% initial TS, solids removal, averaged across the two depths, was generally higher and similar for $CaCO_3$, PAM and the control compared with alum and $MgSO_4$ (Fig 2.2b). While solids removal changed little with time in manure amended with $MgSO_4$ (17-19%) and $CaCO_3$ (28-39%) and in unamended manure (33-36%), it increased from 4% at 0.5 h through 25% at 1 h and 32% at 2 h to peak at 41% after 4 h of settling in PAM-amended manure. Similarly for alum, solids removal increased from 6% at 0.5 h through 11% at 1 h and 16% at 2 h to peak at 31% after 4 h. At the end of the 4 h settling period, solids removal rates in manure containing 5% initial TS were similar for PAM (41%), $CaCO_3$ (39%) and the control (36%) and significantly lower in manure treated with $MgSO_4$ (19%).

Solids removal in manure containing 8% initial TS (mean of the 30- and 60-cm sampling depths) was significantly greater for $CaCO_3$, $MgSO_4$ and the control than alum during the first 4 h of settling except at 0.5 h when amendment differences were not significant (Fig 2.2c). PAM outperformed alum only at the 2-h sampling time and was significantly outperformed by $CaCO_3$ and the control after 4 h of settling. Removal rates after 4 h were -2% (i.e., accumulation) for alum, 9% for PAM, 19% for $MgSO_4$, 33% for the control, and 39% for $CaCO_3$. While no temporal changes in solids removal were observed for alum, removal for the rest of the treatments peaked after 2 h of settling and showed no significant change in samples taken 4 h after the start of settling.

Table 2.3 Amendment type, manure initial solids concentration, depth and settling time effects on net solids removal.

Effect	1% TS[†]	Settling time ≤ 4 h[‡]	90-cm depth[§]
		%	
Amendment			
Control	29	26	26
$CaCO_3$	38	31	35
$MgSO_4$	20	16	18
Alum	27	11	11
PAM	47	26	49
Solid content (%)			
1	-	29	-
5	-	25	-
8	-	12	-
Depth (cm)			
30	33	26	-
60	33	18	-
Time (h)			
0	-	-	-
0.5	29	16	21
1	31	20	24
2	31	23	27
4	34	28	32
8	34	-	33
24	38	-	36
		P- value	
Solid Content (S)	-	0.0005	-
Amendment (A)	0.05	0.01	0.002
Time (T)	0.01	0.02	0.002
Depth (D)	0.86	0.06	-
S × T	-	0.21	-
S × D	-	0.09	-
T × D	0.05	0.57	-
A × S	-	0.05	-
A × T	0.01	0.45	<0.0001
A × D	0.02	0.01	-
A × S × T	-	0.023	-
S × T × D	-	0.4	-
A × S × D	-	0.03	-
A × T × D	0.43	0.24	-
A × S × T × D	-	0.28	-

[†]Solids removal in manure containing 1% initial total solids concentration.

‡Solids removal within the first 4 h settling time for all manure initial total solids concentrations.
§Solids removal at the 90-cm depth in manure containing 1% initial total solids concentration.

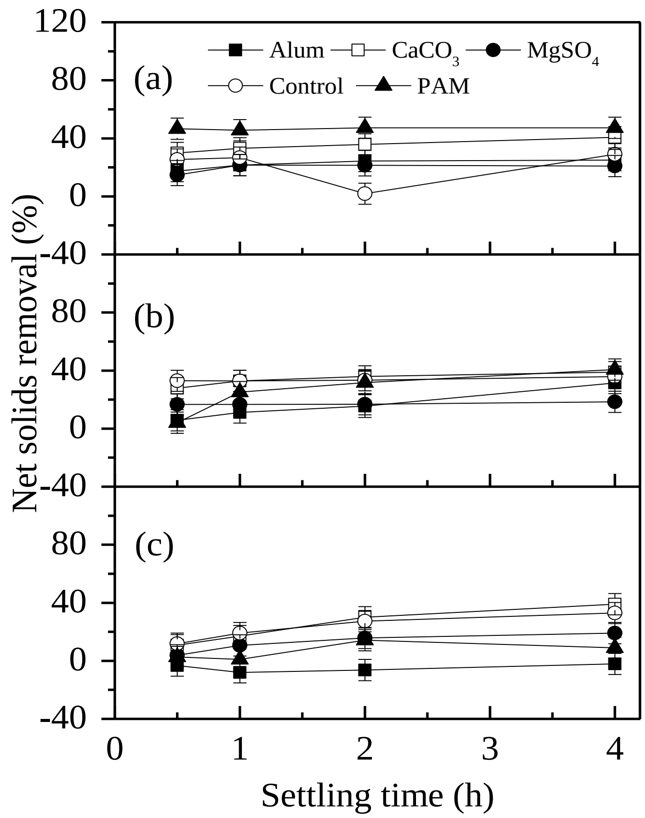

Figure 2.2 Net solids removal in liquid swine manure during the first 4 h of settling as affected by amendment type and settling time for manure containing (a) 1%, (b) 5% and (c) 8% initial solids concentration.

In manure containing 1% initial TS, solids removal from both the 15- to 45- and 45- to 75-cm depth intervals, averaged across sampling times, was greater for PAM (mean 47% for the two depths) than alum (mean 22%), $MgSO_4$ (mean 20%) and control (mean 21%) treatments (Fig 2.3). PAM also resulted in greater solids removal (51%) from the 15- to 45-cm depth interval than alum (21%) and $MgSO_4$ (17%) in manure containing 5% initial TS. In both the 5% and 8% initial TS, solids removal from the 45- to 75-cm depth interval was significantly greater in manure treated with $CaCO_3$ and in the control compared with manure treated with alum and PAM. In fact, there was a net accumulation of solids when manure containing 8% TS was amended with alum (-7%) or PAM (-4%) (Fig 2.3b). The effectiveness of PAM at removing solids from the 15- to 45-cm depth interval was similar for 1% and 5% initial TS concentrations but decreased significantly as the initial TS increased to 8%. In the 45- to 75-cm depth interval, however, PAM effectiveness decreased sharply at 5 and 8% initial TS concentrations compared with 1% initial TS. Alum resulted in a decrease in solids concentration from both the 15- to 45- and 45- to 75-cm depth intervals as the initial TS concentration increased from 5% to 8% TS.

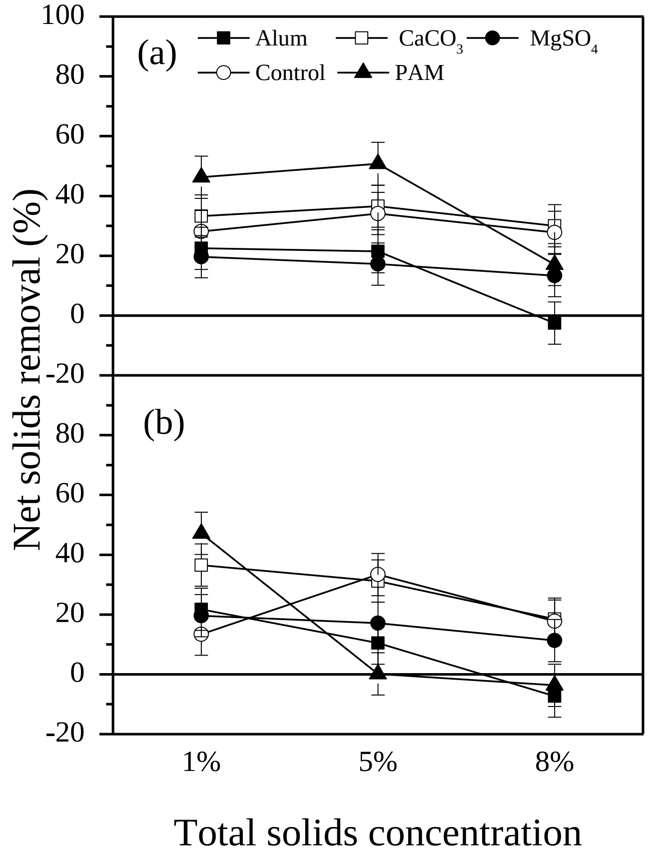

Figure 2.3 Solids removal from the (a) 15- to 45- and (b) 45- to 75-cm depth intervals in liquid swine manure as affected by initial total solids concentration, amendment type, and settling depth.

2.4.3 Solids Removal at the 90 cm Depth and at 1% Initial Solids Concentration

Amendment effects on solids removal, measured at the 90-cm depth for manure containing 1% initial TS (higher initial TS caused clogging of the sampling port), decreased in the order PAM (49%) > $CaCO_3$ (35%) > control (26%) > $MgSO_4$ (18%) > alum (11%) (Table 2.3). The difference in effectiveness was significantly greater for PAM than all the other treatments except $CaCO_3$. Solids removal did not differ significantly among alum, $CaCO_3$, $MgSO_4$ and the control, except at the 0.5- and 1-h sampling times when $CaCO_3$ significantly outperformed alum (which explains the significant ($P < 0.0001$) amendment × time interaction) (Fig. 2.4). Of all treatments, only alum resulted in a significant change in solids removal with sampling time, with the removal increasing from ~-20% after 0.5 h of settling to peak at ~28% after 4 h.

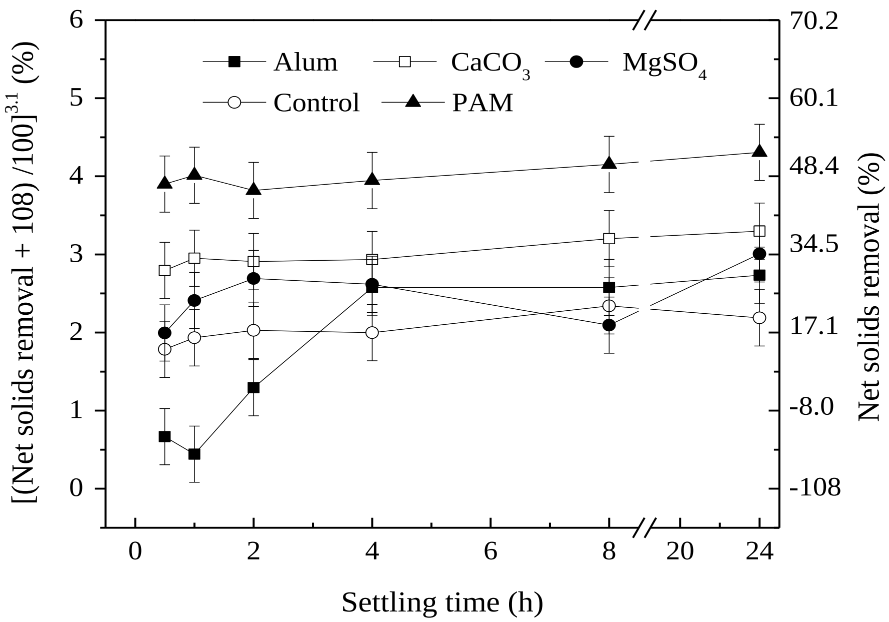

Figure 2.4 Solids removal at the 90-cm depth in manure containing 1% initial total solids as affected by amendment and settling time.

2.5 Discussion

2.5.1 Net Solids Removal

The greater overall effectiveness of PAM, particularly evident in manure containing 1% initial TS, was likely due to its ability to rapidly neutralize the negative charge on suspended particles in liquid swine manure and bridge several suspended solid particles, thus forming larger particles or flocs that settled more easily (Garcia et al., 2007; Masse et al., 2010; Vanotti et al., 2002). The ability of the moderately-charged PAM used in this study to effect such flocculation can be explained by its charge density (Masse et al., 2010). Vanotti and Hunt (1999) reported that cationic PAM formulations with relatively low charge density (approx. 20%), such as the one used in this study, were more effective at solids removal than those with higher charge density (20% to 75%). The reaction of PAM with swine manure containing 1% initial TS occurred immediately after mixing and produced large, dark brown flocs that settled within 4 h, leaving a liquid fraction with a lower suspended solids concentration in the 0- to 75-cm depth interval of the settling column. As sedimentation progressed, solids that had settled out of the 15- to 45-cm depth interval were deposited in the underlying 45- to 75-cm depth interval. The net solids removal in the 45- to 75-cm depth interval, therefore, represented the difference between the export of solids settling out of the layer and the influx of solids from the 15- to 45-cm layer. This resulted in negative solids removal in some cases, such as in manure containing 5% and 8% initial TS, because solids influx was greater than export.

In comparisons made during the first 4 h of settling and involving all three initial TS concentrations, $CaCO_3$ was as effective as PAM at removing solids in manure containing 1% initial TS (Table 2.3 and Fig. 2.2). Calcium carbonate also removed more solids from the 15- to 45-cm depth interval in manure containing 5 and 8% TS when compared with alum and PAM, but was not significantly better than the control treatment.

Swine manure, like activated sludge, comprises of a mixture of negatively charged suspended particles (Christensen et al., 2009; Sievers et al., 1994). A repulsive force develops when the diffuse layer of particles with similar charge move towards each other

(Wang et al., 2005). The repulsive force keeps the particles far apart thereby preventing agglomeration of the particles to form settleable flocs that settle out by gravity (Sievers et al., 1994). Coagulation of the particles occurs when the repulsive force is reduced and the kinetic energy of the particles increased by the presence of coagulants (Thomas et al., 1999; Sievers, 1989). When coagulants such as $MgSO_4$ and $CaCO_3$ are added to swine manure, the positively charged cations (Ca^{2+} and Mg^{2+}) are easily and quickly adsorbed to the negatively charged particle surfaces of suspended solid particles in the manure. Similarly, the aluminum ion (Al^{3+}) get adsorbed to particle surfaces once it is hydrolyzed to form soluble aquometal ions [$Al(H_2O)_6{}^{3+}$] when added to water (Jiang and Graham, 1998; Shin et al., 2008; Wang et al., 2005). These soluble aquometal ions have a strong affinity for the negatively charged manure solids. The adsorbed cations neutralize particle surface charge, thus decreasing or eliminating the repulsive forces that exist between the negatively-charged solid particles (Hjorth et al., 2008; Hjorth et al., 2009). The diffuse layer, which comprises of charged particles and the surrounding cations, gets compressed and becomes thinner, thereby reducing the distance of the charge from the surface of the particle (Sievers et al., 1994). The particles are then able to aggregate due to the close contact between them (Mohamed et al., 2011). Given this background, the high solids removal in $CaCO_3$-treated manure observed in this experiment was likely due to the small hydrated radius of the Ca^{2+} ion (0.412 nm) compared with Mg^{2+} (0.428 nm) and Al^{3+} (0.48 nm) (Tansel et al., 2006). Cations with small hydrated radii and high valence tend to be more strongly adsorbed to negatively charged particle surfaces than those with large radii and low valence (Filep, 1999; Tabatabai and Sparks, 2005).

Results for alum, $CaCO_3$ and PAM from this study differ from several previous studies that reported higher solids removal in manure treated with these amendments (Ndegwa et al., 2001; Power and Flatow, 2002; Vanotti and Hunt, 1999). This may be due in part to differences in experimental protocol and in diet fed to the pigs, which influences the properties of manure used (Powers and Flatow, 2002; Zhang and Lei., 1998). Ndegwa et al. (2001) evaluated alum and ferric chloride [$FeCl_3.6H_2O$] at dosages ranging from 500 to 2000 mg L^{-1} for solids removal in swine manure containing 1% TS using five Plexiglass columns similar in size to those used in the present study. They collected samples from the 0-, 30-, and 60-cm depths after 0.5, 1 and 4 h and reported a 96% removal of suspended solids, after 4 h of settling, in manure treated with 1500 mg L^{-1} alum. The high solids removal in their study was partly due to the high dosage of alum used, which was nearly three times the rate (550 mg L^{-1}) used in the present study for manure containing 1% initial TS.

In the present study, the extent of solids removal in $CaCO_3$–treated manure containing 5 and 8% initial TS was higher when compared with alum at a majority of the sampling times possibly due to the high dosage of $CaCO_3$ used. Powers and Flatow (2002) observed 93 and 71% solids removal by alum and $CaCO_3$, respectively, in swine manure containing 0.24% TS. However, in addition to the low initial TS, the experiment was conducted using 1000 mL Imhoff settling cones for a duration of only 20 min following addition of 625 mg L^{-1} of the coagulants. The authors concluded that, at this dosage, alum and other coagulants [calcium oxide (CaO) and $FeCl_3$] significantly improved solids removal compared with non-amended and $CaCO_3$-treated manure.

Solids removal in swine manure containing 1% initial TS describes a type II clarification (flocculant particles) in which settling is carried out in a relatively dilute suspension (Wang et al., 2005). The 1% TS swine manure is characterized by low concentrations of organic and suspended solids (Gao et al., 1993). The solids increase in mass and settle at a faster rate by falling freely to the bottom of the settling column as flocculation occurs (Robert and Cullum, 1988). The suspended solids or particles in manure move closer to each other and are held in fixed positions relative to each other by interparticle forces as solids concentration increases beyond 1% TS (Tchobanoglous et al., 2003). This results in the solids no longer settling independently of one another, which eventually reduces the settling rate of the solids and leads to poor settling (Robert and Cullum, 1998; Tchobanoglous et al., 2003; Wang et al., 2005; Zhang and Lei, 1998). The concentration of solids in manure containing 8% TS is so high when compared with that containing 1% TS, such that the entire suspension tends to settle as a 'blanket'. This is described as a type III clarification (zone settling) (Wang et al., 2005) and was likely the mechanism of solids settling in high TS manure in the present study.

The overall mechanism of solids settling in the present study is similar to that reported by Robert and Cullum (1998). Their natural sedimentation study using swine manure containing 0.1, 1, and 5% TS in a settling column 1.22-m long by 0.15-m diameter, although conducted for a shorter duration, showed that solids removal after 5, 10, 15, 30, 45, and 60 min was lowest at 5% TS when compared to the 0.1% and 1% TS due to the effect of zone formation. Ndegwa et al. (2001) reported that swine manure solids concentrations above 2% or below 1% affect "natural" gravity sedimentation negatively by reducing the amount of solids removed. Zhang and Lei (1998) utilized settling columns 12.7 cm in diameter and 100 cm in height to separate solids from swine manure varying in initial total solids content (following coagulation using alum and $FeCl_3$ at various optimum dosage) and suggested that the initial TS of manure be limited to 1% if chemical treatment prior to sedimentation is to be used as the only separation process. Their reason was that 1% TS is considered to be in the range of maximum flocculation and zone settling begins when solids concentration is increased beyond 1% TS (Robert and Cullum, 1998; Zhang and Lei, 1998)

The net accumulation (negative removal) of solids observed at the 60-cm depth in 8% TS manure amended with alum and PAM after 4 h can be attributed to the high concentration of solids that accumulated at the lower depth of the settling column (Robert and Cullum, 1998; Van Haandel and Van der Lubbe, 2007). Fast moving solids that have settled out of the upper layer get deposited in the lower layers as the settling process progresses. This eventually results in the lower part of the column having greater solids concentration than initial TS when compared with the upper layer during the first 4 h of settling.

2.6 Conclusions

Gravitational settling without the addition of chemical amendments was capable of removing as much as 30% of suspended solids in liquid swine manure, regardless of the initial solids concentration. Treatment of manure with chemical coagulants (alum, $CaCO_3$ and $MgSO_4$) and a flocculent (PAM) had varying effects on solids/liquid separation. Overall, PAM was the most effective amendment for enhancing solids removal from manure containing 1% initial TS. With this relatively dilute (1%) manure, solids settled and accumulated below the 90-cm depth. Additionally, solids removal from the 0- to 90-cm depth in PAM-treated manure peaked within 0.5 to 1 h of settling.

At higher initial TS concentrations (that is, 5% and 8%), however, resuspension of the solids occurring at settling times greater than 4 h, ostensibly due to microbial activity producing gas bubbles, reduced the effectiveness of PAM. While the threshold initial TS concentration above which resuspension would occur was not established in this study, it is advisable that, if PAM is implemented as the amendment of choice in the solids/liquid separation of swine manure containing at least 5% TS, no more than 4 h retention time should be allowed before the liquid fraction is pumped out. Our results also suggest that, for such high TS manures, the drawout should be at or slightly below the 30-cm depth. An important implication of the shorter retention time (4 h) and shallow drawout for PAM-treated manure is that PAM-treatment may allow for multiple cycles or batches of treatment per day. However, this would in turn require a large settling tank to accommodate the large volumes from the fast turnaround. Nonetheless, this would still be more economical for swine producers compared with other solid-liquid separation techniques, such as centrifugation.

Our results also showed that $CaCO_3$ was the second most effective amendment for removing solids from liquid swine manure containing 1% TS during the first 4 h of settling and in fact slightly outperformed PAM in manure containing 8% initial TS. At all sampling times and initial TS concentrations tested, alum and $MgSO_4$ did not significantly improve solids removal compared with the control.

Since rates tested in manure containing 5 and 8% initial TS were linearly extrapolated from tests using manure containing 1% TS, it is likely that amendment rates used in the higher TS manures were below those required for effective solids removal. Further studies are warranted to definitively identify appropriate amendment rates for initial TS concentrations greater than 1%. Also, there is a need to test these amendments, particularly PAM, in manure containing between 1 and 5% TS so that a TS concentration can be identified above which PAM will be ineffective.

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3 NUTRIENT REMOVAL FROM LIQUID SWINE MANURE DURING CHEMICALLY-ENHANCED SOLIDS-LIQUID SEPARATION

3.1 Abstract

Chemical treatment of swine manure with metal salts and organic polymers has the potential to improve the separation of solids from liquid swine manure by gravity sedimentation. The addition of calcium (Ca) and aluminum (Al) salts could effectively precipitate dissolved phosphorus (P) and also improve the coagulation of suspended solids, which enhances settling. Solids-liquid separation of swine manure results in a P-rich solid fraction and a liquid fraction with a nitrogen (N) to P ratio closely matching crop uptake of these nutrients. Land application of the liquid fraction reduces the risk of P build-up in soils. The objective of this study was to determine the effect of chemical amendments [aluminum sulphate (alum), calcium carbonate ($CaCO_3$), magnesium sulphate ($MgSO_4$) and the polyacrylamide (PAM) Superfloc C-494] on the removal of P, N, Ca and magnesium (Mg) during the gravitational settling of solids in liquid hog manure containing 1%, 5%, and 8% initial total solids (TS). Manure treated with these chemical amendments was placed in separate settling columns (15 cm diam. and 125 cm ht.) with a working volume of 21 L and the mixture allowed to settle. Samples collected from the 30- and 60-cm depths after 0.5, 1, 2, 4, 8 and 24 h of settling were analyzed for pH, electrical conductivity (EC), P, N, Ca and Mg concentrations. After 4 h of settling,

approximately 52% of P in the manure was removed from the 15-to 45-cm depth interval of alum-treated manure containing 1% TS while 48% of the P was removed from PAM-treated manure. In non-amended manure, approximately 53% of the P was removed after 24 h from the 15- to 45-cm layer of manure containing 1% TS while 6% and 11% of the P were removed in non-amended manure containing 5% and 8% initial TS, respectively. After 2 h of settling, alum was more effective at enhancing P removal from manure containing 1% initial TS than that containing 5% and 8% TS. The low P removal in manure containing 5%, and 8% TS suggests that the settling of the suspended solids is hindered, which affects P removal. The addition of chemical amendments did not increase the removal of N and K from swine manure. Similarly, chemical amendment had no significant effect on P removal: removal of P in amended manure was the same as those in the non-amended manure. On the other hand, alum seemed to maintain P removal from the 15- to 45-cm depth interval after 24 h of settling as the initial TS of manure was increased from 1% to 5% and 8%, whereas the other amendments showed a sharp decrease in P removal. These results suggest that gravity settling, even with the addition of chemical enhancers, may have limited effectiveness for removing P from manure of high initial TS concentration, with the possible exception of alum.

3.2 Introduction

Swine manure is a valuable source of plant nutrients, especially phosphorus (P) and nitrogen (N), when utilized properly and in an environmentally sustainable manner (Hodgkinson et al., 2002; Novak et al., 2000). In 2006, the 180 million tonnes of livestock manure generated in Canada contained approximately 300,000 tonnes of P and

1 million tonnes of N (Statistics Canada, 2006). Swine operations in the Canadian Prairies generate large quantities of manure annually, which raises a disposal concern for producers (Choudhary et al., 1996). The nitrogen-to-phosphorus ratio (N:P ratio) of manure is often smaller than for crop requirements, which increases the risk of P losses to the environment following land application of manure (Bailey and Buckley, 1998; Miller et al., 2011). Swine manure is typically applied repeatedly on agricultural land based on agronomic N rate, which often results in a build-up of both P and potassium (K) in soils (Novak et al., 2000). Phosphorus can be lost from soils with elevated soil test P to surface and ground water through leaching and surface runoff following precipitation and snowmelt (Wright et al., 2010; Little et al., 2007). The quality of water bodies such as streams, lakes and rivers gradually degrades through eutrophication due to the presence of excess nutrients, posing a serious threat to both aquatic life and human health (Allen and Mallarino, 2008).

Separating swine manure into a P-depleted, N-rich liquid fraction and a P-rich solids fraction prior to land application would increase the N:P ratio of the liquid fraction and also lower the cost of nutrient transport (Hjorth and Christensen, 2008; Hjorth et al., 2010; Walker et al., 2010). Available mechanical separators are not efficient in removing the fine suspended solids that contain organic nutrients in liquid swine manure (Cristina et al., 2008; Vanotti and Hunt, 1999; Zhang and Western, 1997). Treatment with flocculants, such as polyacrylamide (PAM), and coagulants prior to mechanical removal or gravity settling of the solids has the potential to improve solid-liquid separation, thus differentially concentrating P and N in the separated fractions (Powers and Flatow, 2002; Rodriguez et al., 2005; Vanotti et al., 2002).

Several studies with coagulants, such as Al, Ca and iron (Fe) salts, have demonstrated the effectiveness of these chemicals in removing nutrients from liquid manure by inducing the aggregation of the fine suspended solid particles (Krumpelman et al., 2005; Nahm, 2005; Power and Flatow, 2002). Power and Flatow (2002) tested aluminum sulphate [alum, $Al_2(SO_4)_3$], $CaCO_3$, $FeSO_4$, CaO, and $FeCl_3$ in swine manure containing 0.24% TS using 1-L Nalgene Imhoff settling cones. The coagulants were applied at rates of 40, 250, and 625 mg L^{-1}. After chemical addition, manure samples were mixed for 2 min and allowed to settle for 20 min after which samples were taken from the supernatant and the settled solids for chemical analysis. Results from these experiments showed that, of the five coagulants, only alum significantly improved solids and P removal from the swine manure samples tested. Application of 625 mg L^{-1} alum resulted in the removal of 91% of P compared with 74% removal for 250 mg L^{-1} alum.

Polymers such as PAM are also commonly used to flocculate suspended solids prior to sedimentation or screening. Polyacrylamides are moderate to high molecular weight, long-chain, water-soluble polymers (Truis and Cheryl, 1991; Vanotti et al., 2002). They are effective at destabilizing suspended, charged particles by adsorbing onto them and forming bridges between several suspended solid particles (Hjorth et al., 2008; Vanotti and Hunt, 1999). Flocculation of manure through PAM treatment results in agglomeration of the smaller particles or fine suspended solid particles into larger flocs that separate from the liquid more easily. Highly charged cationic PAM has been reported to enhance solid-liquid separation of swine manure better than the anionic or neutral PAMs or alum (Garcia et al., 2007; Vanotti and Hunt, 1999).

In most previous studies, the effectiveness of these chemical amendments was evaluated using high dosages of the chemicals in manure with low (≤ 1%) total solids (TS) concentration. Additionally, the settling tests were performed in beakers or 1-L Imhoff cones, which are used for standard settleable solids tests (APHA et al., 2005). Several of these studies have reported higher nutrient removals, especially for P and N, from swine manure following chemical treatment, which may not necessarily be observed when conducted in large settling columns or settling basins in the field. Further research using settling columns with depths similar to commercial-scale settling tanks is therefore needed to more accurately examine the extent of chemically-enhanced solids and nutrient removal from liquid swine manure.

The objectives of this research were to (1) compare the effects of various chemical amendments on the removal of P, N and other nutrients from liquid swine manure and (2) investigate the effects of varying initial total solids concentrations of swine manure on the removal of these nutrients.

3.3 Materials and Methods

3.3.1 Manure Collection and Preparation

Chemical amendment effects on nutrient separation from liquid swine manure were evaluated using custom-made settling columns. Swine manure was collected from a commercial swine operation near Niverville, MB. The manure was from weanling to finisher pigs raised on slatted floors and fed a commercial feed mixture supplemented with phytase. Two manure batches were collected for the study. The first batch, with a solids concentration of 3%, was collected directly into twenty, 20-litre plastic containers from an effluent pipe discharging into a lift station on the concrete floor. Since we were also interested in testing the amendments at manure TS greater than 3%, a second batch was collected by scrapping semi-solid manure from the pen floor just before the manure was flushed into pits.

Samples were taken from both batches and stored at -19°C until laboratory analysis as described in Section 3.3.4. The rest of the manure in the first batch was diluted with tap water to attain a solids concentration of 1% while the second batch was diluted to achieve solids concentrations of 5% and 8%. The diluted manure was stored at 4°C until the start of the sedimentation experiment.

3.3.2 Chemical Amendments

The amendments tested were aluminum sulphate [alum, $Al_2(SO_4)_3 \bullet 13H_2O$], $CaCO_3$, $MgSO_4$ and PAM. Alum was included because it is commonly used to precipitate P in municipal wastewater and has been reported to reduce P concentration and enhance solids removal in liquid swine manure (Vanotti and Hunt, 1999). The PAM used was a commercially available dry formulation (Superfloc C-494, Kemira Water Solutions, Inc., Lakeland, FL). Superfloc C-494 is a moderately charged (19 mole % charge density), high-molecular weight, cationic powder containing about 93% active polymer and is a copolymer of acrylamide and methyl chloride quaternary ammonium salt of dimethylaminoethyl acrylate (Garcia et al., 2007; Vanotti and Hunt, 1999). Amendment concentrations used in the experiment were based on previous studies (Power et al., 2002; Vanotti and Hunt, 1999; Zhang et al., 1998) (Table 3.2).

3.3.3 Sedimentation Experiment

Gravity settling tests were performed in custom-made cast acrylic tube columns (15 cm in diameter and 125 cm in height to closely approximate the depth of a typical commercial-scale settling tank). Manure diluted to three initial total solids contents, as described in Section 3.3.3, was treated with the four amendments described above. Immediately after adding the chemicals (time 0), manure samples were collected into 50-mL centrifuge tubes while the rest of the manure was carefully transferred into settling columns, allowing for 5 cm between the top of the column and the surface of the fluid, resulting in a 120-cm column of manure. Five columns were tested at a time, four of which contained amended manure while the fifth contained non-amended (control) manure for comparison. This setup was replicated three times. Fifty-milliliter samples were taken after 0.5, 1, 2, 4, 8 and 24 hours from the 30-, and 60-cm depths (measured from the top of the manure column). All samples were stored in a freezer at -19 °C until laboratory analysis.

Table 3.1 Characteristics of the two batches of raw swine manure used in the sedimentation experiment.

Parameter†	Batch 1	Batch 2
Total solid (%)	3	17
pH	6.1	6.8
Electrical Conductivity (dS m^{-1})	5.1	8.5
Total P (g Kg^{-1})	13	12
Total N (g Kg^{-1})	62	58
Mg (g Kg^{-1})	11	10
Ca (g Kg^{-1})	15	16
K (g Kg^{-1})	22	19
N:P ratio	4.74	4.97

†Total solid, pH, and electrical conductivity on fresh weight; total P, total N, Mg, Ca, K and N:P ratio on dry weight basis.

Table 3.2 Dosage of chemical amendments in swine liquid manure of varying solids content.

Total solids conc. (%)	**Amendment application dosage (mg L^{-1})†**			
	$CaCO_3$	**$MgSO_4$**	**Alum**	**PAM ‡**
1	2856	3256	549	122
5	14548	16801	3999	636
8	21038	25245	6083	946

† Concentration of amendments (mg L^{-1}) in swine manure in the settling columns.
‡ Cationic PAM (Superfloc C494, Kemira Water Solutions, Inc., Lakeland, Florida).

3.3.4 Laboratory analysis

Frozen manure samples were thawed and allowed to come to room temperature (21±2°C) before analysis. Sample temperature, pH and electrical conductivity (EC) were measured using a digital pH/conductivity meter (Accumet AP85, Fisher Scientific, Singapore). In manure containing 17% initial TS, EC and pH were measured in a 1:2 manure to water mixture while measurements were taken directly in 25-mL liquid swine manure containing 3% TS (Peters et al., 2003). Samples were also analyzed for total P (TP), total Kjeldahl N (TKN), Ca, Mg and K concentrations. Total P, Ca, Mg and K concentrations (Table 3.1) were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; Vista-MPX, Varian Analytical Instruments, Mulgrave, Victoria, Australia) following wet oxidation (Akinremi et al., 2003). Total Kjeldahl N was measured with an autoanalyzer (AA II, Technicon, Tarrytown, NY) using the colorimetric automated phenate method (APHA et al., 2005). Total suspended solids concentration was determined for all samples using standard methods (APHA et al., 2005).

3.3.5 Calculations

Nutrient removal from a given volume in each depth interval (layer) was calculated for each sampling time as the difference between the initial nutrient mass in the layer minus the nutrient mass at the sampling time, expressed as a percentage of initial nutrient mass. For example, for P:

$$\text{P removal (\%)} = [1 - (P_i / P_0)] \times 100$$

where P_i is the mass (g) of P settled out of a given depth interval (e.g., the 15- to 45-cm layer) and P_0 is the mass of P (g) in the same layer before settling commenced (Power and Flatow, 2002).

The 30-cm depth was considered as the drawout for the 120-cm manure column and nutrient removal was calculated at this depth, particularly for manure containing 5% and 8% initial TS. For manure containing 1% initial TS, the 90-cm depth was also considered a drawout. Since nutrients settling out of the upper layers were deposited in the layers below, negative removals were recorded in those cases where influx of a given nutrient into the layer from layers above was greater than the export of nutrients out of the layer, representing nutrient accumulation in the layer.

3.3.6 Statistical Analysis

Because preliminary tests indicated minimal effects of $CaCO_3$ and $MgSO_4$ on nutrient removal, laboratory analyses of samples from these treatments were not carried out except at 24 h of settling. Nutrient removal results are therefore presented only for PAM, alum and the control treatment.

Nutrient removal data (positive or negative as described above) calculated for each depth at different sampling times were analyzed using the MIXED procedure for repeated measures (Littell et al., 2000; SAS Institute, 2008), with sampling time as the repeated factor. The spatial power [SP(POW)] covariance structure was used in the model to account for unequal sampling time intervals. Initial manure TS, amendment type, sampling time and sampling depth were modeled as fixed effects while replication and its interactions with fixed effects were random effects. For comparisons involving PAM-treated manure containing 5 and 8% initial TS, nutrient removal data were analyzed only for settling times up to 4 h because data for later samplings were confounded by the re-suspension of previously settled, flocculated solids in the PAM treatments. Additional analyses excluding the PAM treatment were performed for all sampling times and initial TS concentrations. Since re-suspension was not observed in manure containing 1% TS, a complete analysis (i.e., including all amendments (except for $CaCO_3$ and $MgSO_4$ treatment) and sampling times) was performed for all depths for this manure. For all analyses, treatment differences were deemed significant if $P < 0.1$ using the Tukey method. Results for N:P ratio, pH and EC are presented for all initial TS concentrations and two depths (30 and 60 cm). Nutrient removal (P, N, Ca, Mg and K) data are presented for four scenarios: (i) for the 1% initial TS concentration, all settling times and two depths (30 and 60 cm) were assessed; (ii) for all initial TS concentrations, settling was assessed for the first 4 h of sedimentation and two depths (30 and 60 cm); (iii) for all initial TS concentration, settling only after 24 h of sedimentation and two depths (30 and 60 cm) was assessed excluding PAM; and (iv) also for the 1% initial TS, the 90 cm depth was analyzed separately to represent the drawout and also because three depth levels could not be analyzed as the second of two repeated measures since time (first repeated factor) intervals were unequal.

3.4 Results

3.4.1 Net P removal at the 30- and 60-cm Depths at 1% Initial Total Solids Concentration

Net P removal during the sedimentation experiment was not significantly affected by amendment type (P = 0.97). However, for each amendment, P removal varied with sampling time, as indicated by the significant (P = 0.02) three-way interaction (Table 3.3). In non-amended manure, P removal from the 45- to 75-cm layer increased from 45% at 2 h to approximately 49% after 4 h of settling in manure containing 1% TS (Fig 3.1). While there was no amendment effect on P removal, the rate of P removal from both the 15- to 45- and 45- to 75-cm depth intervals in the non-amended manure continued to increase throughout the sampling period peaking at 53 and 55% respectively, after 24 h. Phosphorus removal from the 15- to 45-cm layer (49%) of alum-treated manure was significantly greater at 0.5 h sampling time compared with the 15- to 75-cm layer (38%).

Table 3.3 Amendment type, depth and settling time effects on net nutrient removal, pH and EC in manure containing 1% initial solids concentration.

Effect	**TP**	**TKN**	**Ca**	**Mg**	**K**	**pH**	**EC**
		% net nutrient removal.					**dS m^{-1}**
Amendment							
Control	47	13	37	50	0.47	7.0	9.8
Alum	49	-5.75	45	35	2.56	6.9	10.6
PAM	47	8.95	50	42	-4.66	7.0	10.0
Ca CO_3	-	-	-	-	-	7.1	10.2
$MgSO_4$	-	-	-	-	-	6.8	12.4
Depth (cm)							
30	49	6.56	44	43	-0.03	7.0	10.4
60	47	4.02	43	42	-1.06	7.0	10.5
Time (h)							
0	-	-	-	-	-	6.9	10.4
0.5	43	8.51	39	39	1.36	7.0	10.3
1	46	7.36	41	41	-1.63	7.0	10.5
2	48	6.86	43	41	-1.12	7.0	10.5
4	50	6.15	45	45	-0.42	7.0	10.5
8	50	3.14	45	44	-0.93	7.0	10.5
24	51	-0.30	48	45	-0.54	7.0	10.6
			P- value				
Amendment (A)	0.97	0.68	0.59	0.64	0.54	<0.001	<0.001
Time (T)	<0.001	0.37	<0.001	<0.001	0.45	<0.001	0.01
Depth (D)	0.23	0.49	0.61	0.45	0.30	0.01	0.08
T × D	0.50	0.45	0.70	0.55	0.98	0.25	0.6
A × T	<0.001	0.08	0.002	<0.001	0.27	0.001	0.01
A × D	0.54	0.97	0.88	0.60	0.96	0.44	0.04
A × T × D	0.02	0.67	0.41	0.01	0.04	0.62	0.99

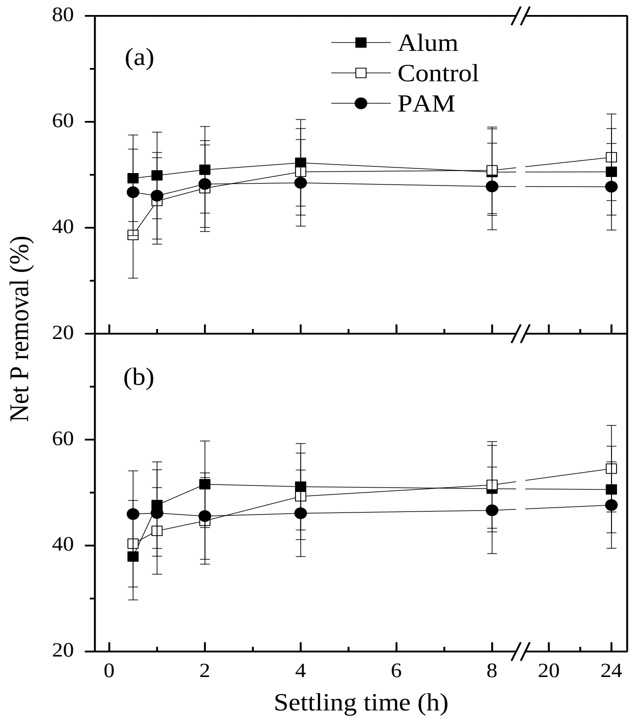

Figure 3.1 Net P removal in the (a) 15- to 45- and (b) 45- to 75-cm layers in liquid swine manure as affected by amendment type, sampling depth and settling time.

3.4.2 Net N, Ca, Mg and K Removal at the 30- and 60-cm Depths at 1% Initial Total Solids Concentration

There was a significant amendment x time interaction for change in N (P = 0.08) and Ca (P = 0.002) while the amendment x time x depth interaction was significant for change in Mg (P = 0.01) and K (P = 0.04) concentration in manure containing 1% initial TS (Table 3.3). However, the Tukey test was not powerful enough to detect any differences in pairwise comparisons.

3.4.3 Net Phosphorus removal at the 30- and 60-cm Sampling Depths During the First 4 h of Sampling

Generally, P removal was much greater for the 1% TS than for 5% and 8% TS. The effect of time was modest, with the differences between the 5% and 8% TS in the PAM-amended manure from the 15- to 45- cm layer widening after 1 h. Phosphorus removal from liquid swine manure (net accumulation if negative), averaged across initial TS concentrations, depths and sampling times, was not significantly affected by amendment type ($P = 0.75$). However, for each amendment, P removal varied with initial TS, depth and sampling time, as indicated by the significant ($P < 0.08$) four-way interaction (Table 3.4). Phosphorus removal from the 15- to 45-cm layer of alum-amended manure containing 1% TS was greater than P removal from the 5% TS manure for the entire settling period and the 8% TS manure for all but the 1-h sampling time (Fig 3.2a). Phosphorus removal in alum-amended manure containing 1% TS was 52% after 4 h while 17% and 1% P were removed from manure containing 5 and 8% TS, respectively. In the 45- to 75-cm depth interval, P removal was significantly greater in alum-treated manure and was significantly greater for 1% initial TS than the 5 and 8% initial TS at all sampling times (Fig 3.2b). Alum in fact resulted in net accumulation of P in the 45- to 75-cm layer for both the 5 and 8% TS manure after 4 h.

Similarly, P removal from the 15- to 45-cm layer was significantly greater in PAM-amended manure containing 1% TS compared with that containing 5% TS throughout the settling period and for the 8% TS only within the first 0.5 h of settling (Fig 3.2c). After 4 h of settling, PAM application resulted in the removal of 48% of P from the

15- to- 45-cm layer of manure containing 1% TS and 13% from manure containing 5% TS. A similar trend was observed in the 45- to 75-cm layer, where P removal was also significantly greater at the 1% TS when compared with both the 5 and 8% TS concentrations throughout the settling period (Fig 3.2d). PAM application, however, resulted in the net accumulation (negative removal) of P in the 45- to 75-cm depth after 4 h of settling as the initial TS of the manure was increased to 5%.

Phosphorus removal from the 15- to 45-cm layer in non-amended manure containing 1% TS was significantly higher than that in manure containing 5% TS at all but the 0.5-h sampling time and manure containing 8% TS for the entire settling period (Fig 3.2e). Approximately 51% of P was removed with the solids fraction from the 15- to 45 cm layer after 4 h in manure containing 1% TS, while 2% and 6% P were removed from the same layer in manure containing 5% and 8% TS, respectively. Removal of P from the 45- to 75-cm layer was also higher in 1% TS swine manure compared with manure containing 5 and 8% TS (Fig 3.2f).

Table 3.4 Amendment type, manure initial solids content, depth and settling time effects on net nutrient removal, N:P ratio, pH and EC during the first 4 h of settling.

Effect	TP	TKN	Ca	Mg	K	N: P	pH	EC
		% net nutrient removal.						**dS m^{-1}**
Amendment								
Control	18	-3.09	19	19	-0.67	5.3	6.6	11.2
Alum	16	-10.28	8.99	8.59	-0.73	5.7	6.3	11.7
PAM	21	10	35	21	-1.68	5.3	6.7	11.1
$CaCO_3$	-	-	-	-	-	-	6.6	11.5
$MgSO_4$	-	-	-	-	-	-	6.4	15.4
Solid content (%)								
1	47	7.24	42	41	-0.45	7.1	7.0	10.4
5	3.20	-4.29	17	1.77	1.52	5.0	6.1	14.4
8	4.98	-6.30	4.40	5.10	-4.15	4.8		
Depth (cm)								
30	20	1.23	24	17	-0.79	5.4	6.5	11.9
60	17	-3.46	18	15	-1.27	5.5	6.5	11.9
Time (hr)								
0	-	-		-	-	4.7	6.5	11.8
0.5	16	-3.16	17	14	-0.23	5.7	6.5	11.8
1	18	-2.40	20	15	-2.09	5.7	6.5	12.0
2	19	-1.21	22	16	-2.06	5.7	6.6	12.0
4	20	2.32	25	19	0.26	5.5	6.5	12.0
				P- value				
Solid Content (S)	<0.001	0.19	0.06	<0.001	0.37	0.01	0.020	0.001
Amendment (A)	0.75	0.05	0.09	0.15	0.94	0.1	<0.001	<0.001
Time (T)	0.01	0.13	0.003	0.05	0.38	<0.001	0.003	0.04
Depth (D)	0.01	0.003	0.05	0.01	0.59	0.07	0.01	0.77
S × T	0.35	0.15	0.49	0.3	0.95	<0.001	0.11	0.52
S × D	0.68	0.02	0.19	0.62	0.18	0.01	0.20	0.15
T × D	0.03	0.03	<0.001	<0.001	0.96	0.48	0.25	0.3
A × S	0.40	0.80	0.001	0.77	0.69	<0.001	<0.001	<0.001
A × T	0.81	0.16	0.23	0.91	0.45	0.001	0.08	<0.001
A × D	0.21	0.01	0.14	0.05	0.29	0.02	0.23	0.50
A × S × T	0.49	0.16	0.16	0.12	0.52	0.01	<0.001	0.98
S × T × D	0.04	0.10	0.04	0.42	0.55	0.03	0.29	0.68
A × S × D	0.23	0.05	0.55	0.23	0.43	0.005	0.93	0.62
A × T × D	<0.001	<0.001	<0.001	<0.001	0.02	0.07	0.86	0.3
A × S × T × D	0.08	<0.001	<0.001	0.01	0.42	0.06	0.86	0.28

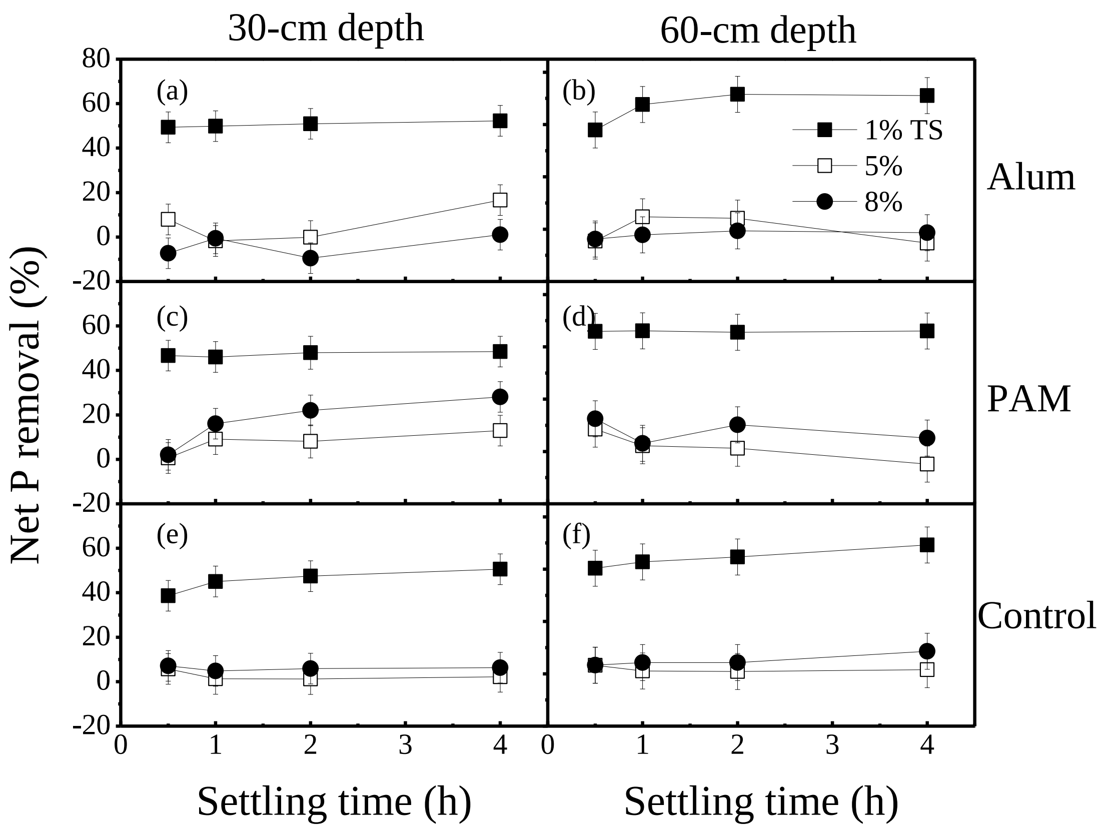

Figure 3.2 Net P removal in liquid swine manure as affected by initial solids concentration, settling depth, settling time and amendment.

3.4.4 Net Nitrogen Removal at the 30- and 60-cm Sampling Depths During the first 4 h of Sampling

Nitrogen removal from the liquid fraction differed significantly ($P = 0.05$) among amendments; however, amendment differences varied with initial TS concentration of the manure, sampling depth, and sampling time ($P < 0.001$ for the four-way interaction; Table 3.4). PAM application increased N removal from the 15- to 45-cm layer in manure containing 5% TS from ~-16% at 0.5 h to about 24% N removed after 1 h of settling (Fig 3.3). Nitrogen removal from the 15- to 45-cm layer of PAM-treated manure containing 5% TS was significantly greater at all but the 0.5 h sampling time compared with the 45- to 75-cm layer. In fact, net accumulation (negative removal) of N was observed in the 45- to 75-cm layer in PAM-amended manure containing 5% TS.

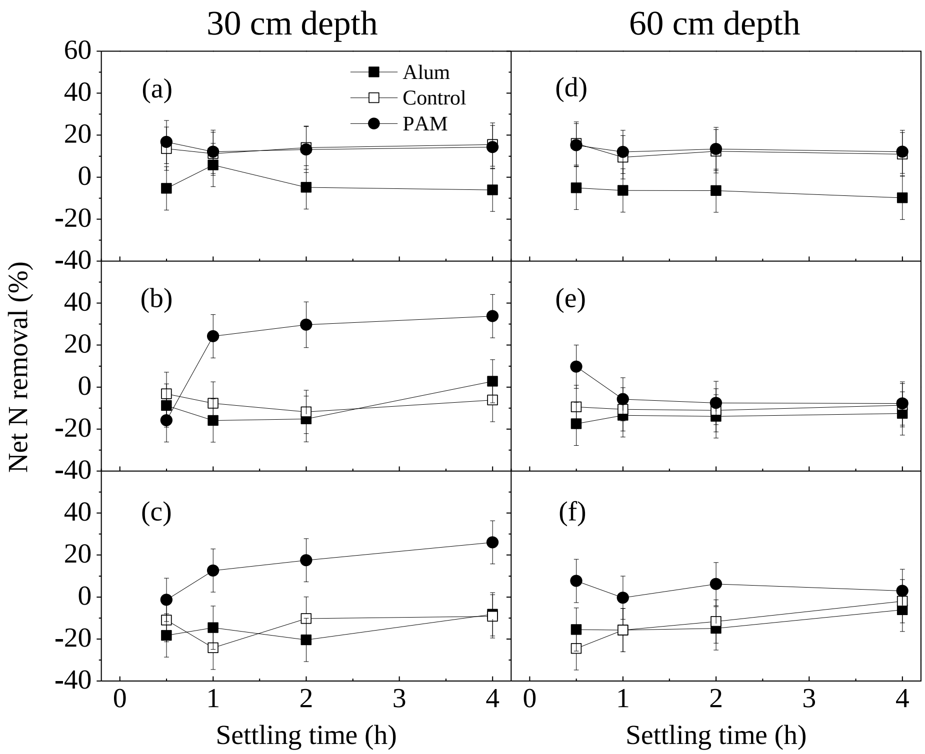

Figure 3.3 Net N removal in liquid swine manure as affected by amendment type, settling depth and settling time in manure containing 1% (a and d), 5% (b and e) and 8% (c and f) initial solids.

3.4.5 Net Calcium Removal from the 30- and 60-cm Sampling Depths during the First 4 h of Sampling

Removal of Ca from the liquid fraction differed significantly ($P = 0.09$) among amendments; however, amendment differences varied with initial solids concentration, sampling depth, and time, as indicated by the significant ($P < 0.001$) four-way interaction (Table 3.4). With the exception of the 0.5 h sampling time, Ca removal from the 15- to 45-cm layer in manure containing 5% and 8% TS was significantly higher with PAM compared with the alum and control treatments (Fig. 3.4). In PAM-amended manure, Ca removal from the 15- to 45- and 45- to 75-cm layers peaked at approximately 50% after 0.5 h of settling in manure containing 1% TS. In manure containing higher TS, Ca removal from the two layers also peaked at ~50%, but this peak took longer to attain as initial manure TS increased (Fig. 3.4). Removal rates from the 45- to 75-cm layer in PAM-treated manure containing 5% and 8% TS were 25% or smaller. On average, alum treatment resulted in net Ca accumulation in manure containing 8% TS and, to a lesser extent, that containing 5% TS.

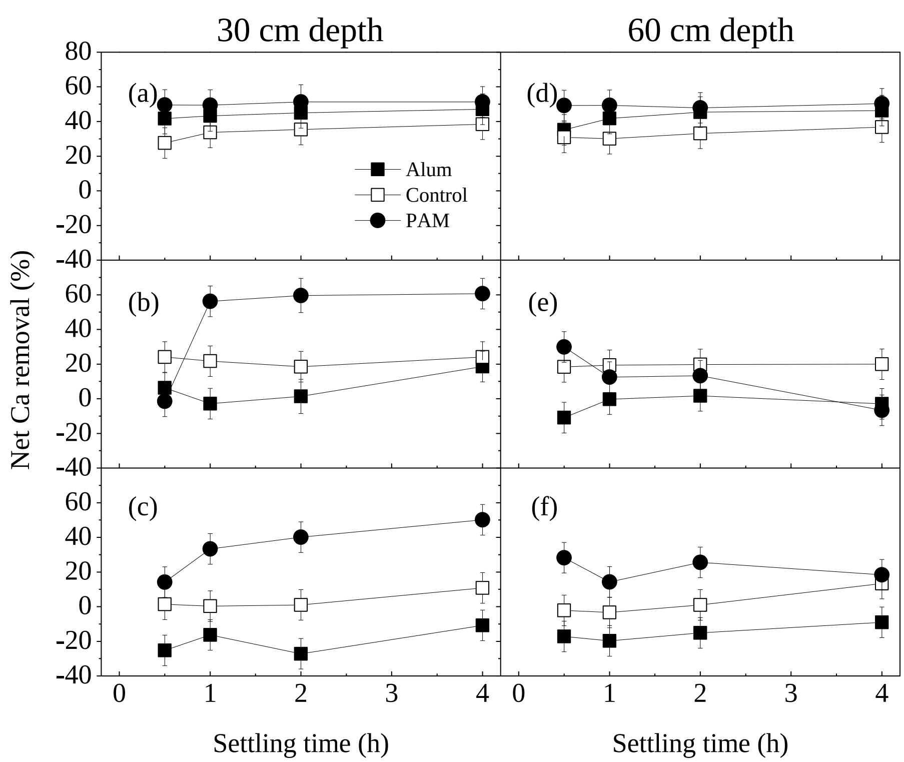

Figure 3.4 Net Ca removal in liquid swine containing 1% (a and d), 5% (b and e) and 8% (c and f) initial solids as affected by amendment type, settling depth and settling time.

3.4.6 Net Magnesium Removal at the 30- and 60-cm Sampling Depths during the first 4 h of Sampling

Magnesium removal during the sedimentation experiment was not significantly affected by amendment type (P = 0.15). However, for each amendment, Mg removal varied with initial manure TS, sampling depth, and settling time, as indicated by the significant (P = 0.01) four-way interaction (Table 3.4). Throughout the sampling period, Mg removal from both the 15- to 45- and 45- to 75-cm layers was significantly greater in amended and non-amended manure containing 1% TS compared with manure containing 5% and 8% TS (Fig.3.5). In the 8% TS manure, Mg removal increased steadily with settling time in manure amended with PAM, whereas no temporal trends were observed for alum and the control.

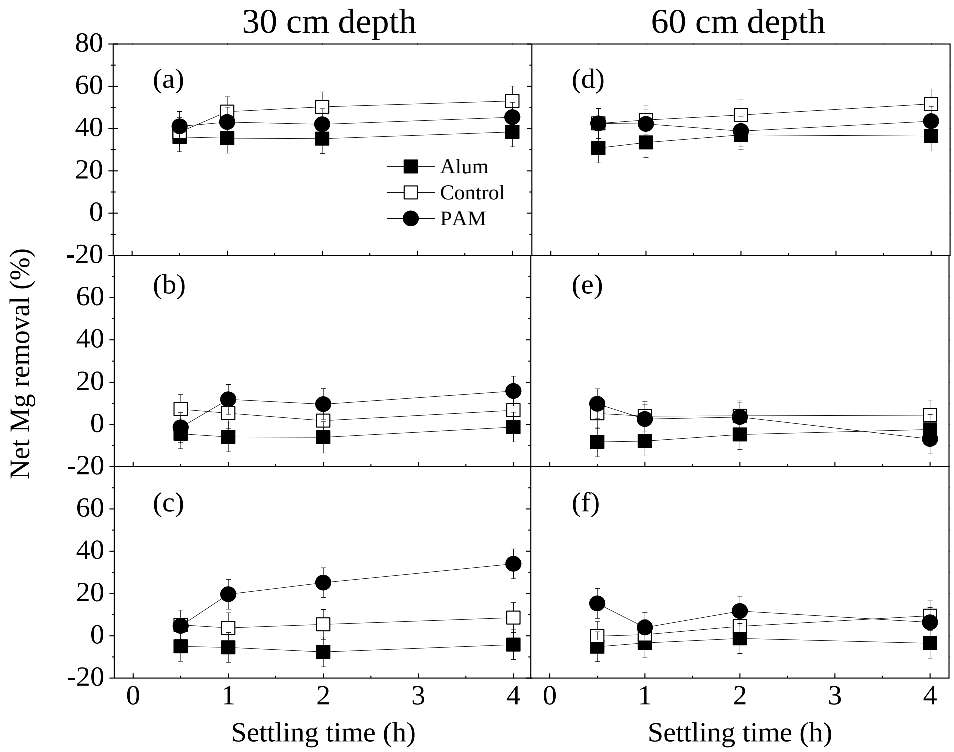

Figure 3.5 Net Mg removal in liquid swine manure as affected by amendment type, settling depth and settling time in manure containing 1% (a and d), 5% (b and e) and 8% (c and f) initial solids.

3.4.7 N:P ratio of Manure

Amendment effect on the N:P ratio of manure was significant (P = 0.1) and depended on initial TS, sampling depth and settling time, as indicated by the significant (P = 0.06) four-way interaction (Table 3.4). All amendments (including the control) showed a temporal increase in the N:P ratio in both the 15- to 45- and 45- to 75-cm layers during the first 0.5 h of settling, except in manure containing 5% TS, particularly in the 15- to 45-cm layer (Fig. 3.6) . While no significant change in the N:P ratio occurred in the alum and control treatments after 0.5 h of settling, there was a significant decrease in the ratio in PAM-amended samples taken from the 30-cm depth (representing the 15- to 45-cm layer) in manure containing 5% TS at 0.5

h after sampling or later compared to those taken earlier (Fig. 3.6b). As settling time increased, treatment differences widened in manure containing 5% TS in the 15- to 45-cm layer, with PAM having the lowest N:P ratio compared with alum and the non-amended manure after 4 h.

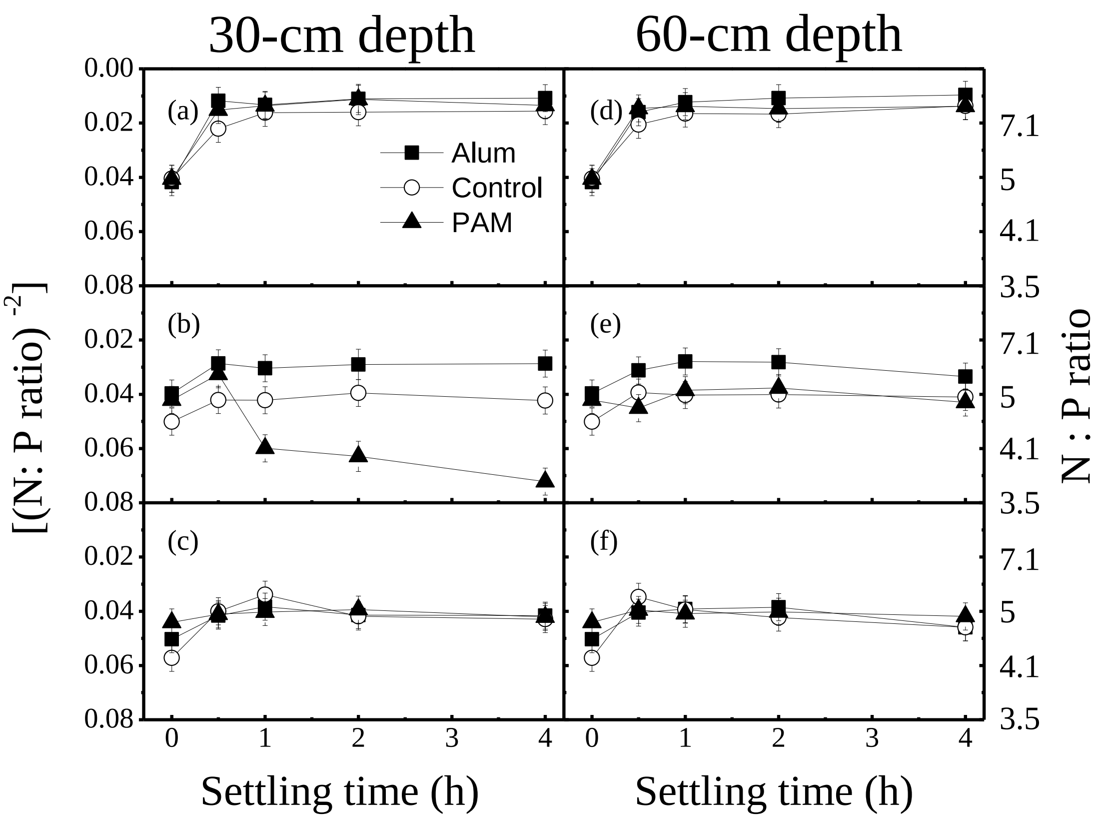

Figure 3.6 Nitrogen to phosphorus (N:P) ratio of settled liquid swine manure as affected by amendment type, settling time and sampling depth in manure containing 1% (a and d), 5% (b and e) and 8% (c and f) total solids.

3.4.8 Manure pH

Amendment effects on manure pH, assessed only for manure containing 1% and 5% TS, were significant ($P < 0.001$) but varied with initial manure TS and sampling time (Table 3.4). Generally, the pH was greater for all amendments in manure containing 1% TS than in the 5% TS manure during the entire sampling period (Fig.3.7). While differences among amendments were small and non-significant for the 1% TS, alum application resulted in significantly lower pH compared with all the other amendments except $MgSO_4$.

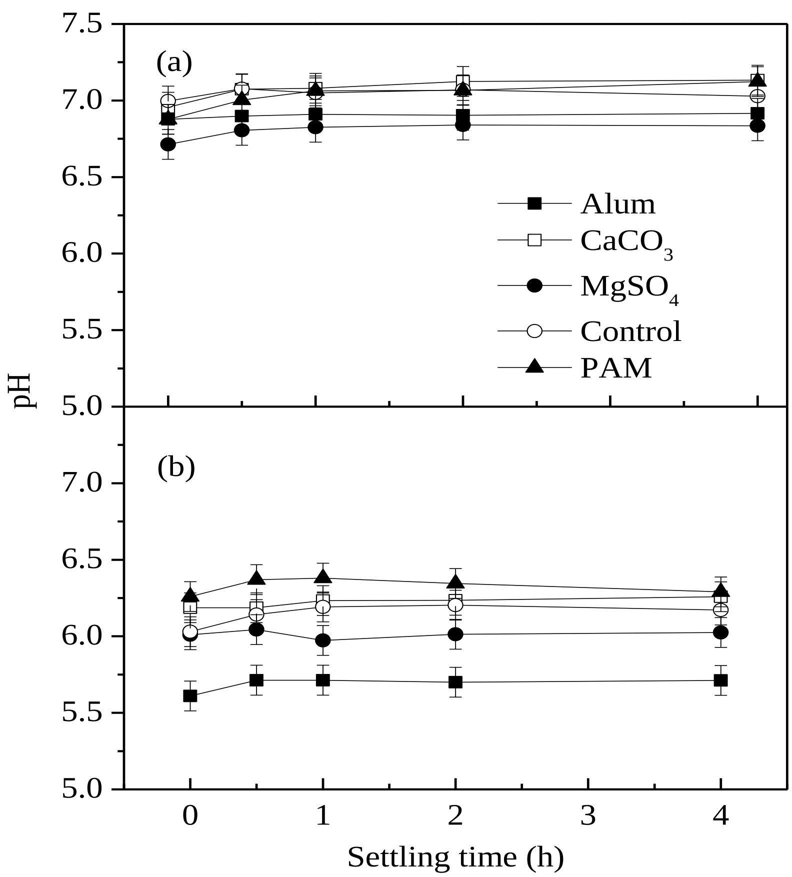

Figure 3.7 Change in pH of manure containing 1% (a) and 5% (b) total solids as affected by amendment type and settling time.

3.4.9 Electrical Conductivity

Amendment x time ($P < 0.0001$), and amendment x initial solids content ($P < 0.0001$) interactions were significant for EC (Table 3.4). Across all sampling times, EC was significantly higher in $MgSO_4$-amended manure compared with all the other amendments (Fig.3.8). Generally, PAM resulted in the lowest EC, which was significantly lower than that in alum-amended manure at all but the initial (time 0) sampling time, and that in $CaCO_3$-treated manure at time 0 and at the 1-h sampling time.

Electrical conductivity, assessed for the 1% and 5% TS only and averaged across sampling times and depths, was significantly greater in $MgSO_4$-amended manure compared with all other amendments (Fig.3.9). In manure containing 1% TS, alum also increased EC relative to both PAM and the control.

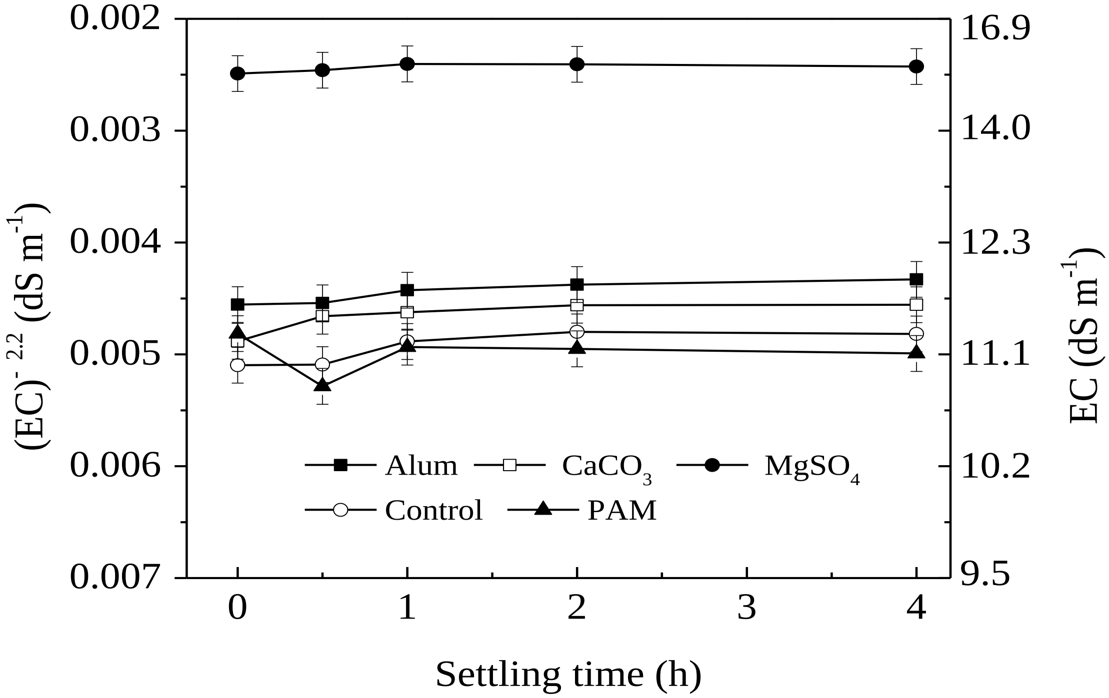

Figure 3.8 Change in electrical conductivity (EC) of liquid swine manure as affected by amendment type and sedimentation time.

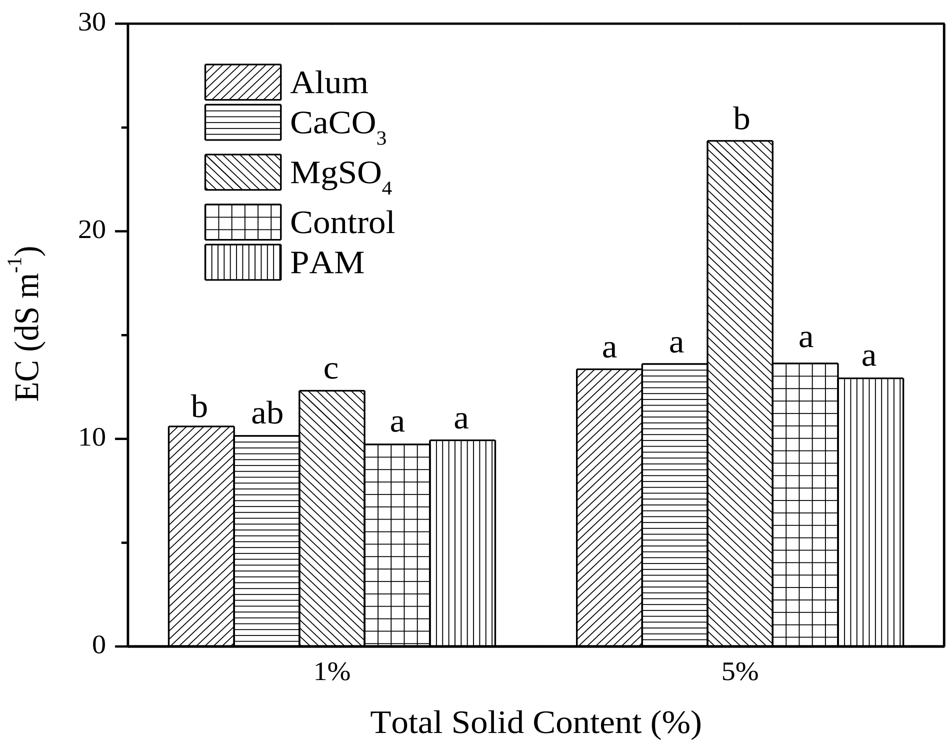

Figure 3.9 Change in electrical conductivity (EC) of swine manure as affected by amendment type and initial solids content of manure.

3.7.10 Net P Removal after 24 h of Settling

Because of confounding effects from re-suspension of separated solids in PAM-amended manure containing 5% and 8% initial TS, PAM effects were not assessed in samples taken after 24 h. Data for this sampling time are therefore presented only for alum, $CaCO_3$, $MgSO_4$, and the control. At the end of the 24-h sedimentation period, manure P removal did not differ significantly among amendment treatments (P = 0.6). However, for each amendment, P removal varied with initial manure TS and sampling depth, as indicated by the significant (P = 0.01) three-way interaction (Table 3.5). While P removal in the 15- to 45-cm layer decreased significantly in manure treated with $CaCO_3$ and $MgSO_4$ and in non-amended manure as initial manure TS increased from 1% to 5%, only a slight but steady decrease in P removal was observed in the alum treatment (Fig. 3.10). Although the amendment main effect was not significant, alum removed much more P (45%) from the 15- to 45-cm layer in manure containing 5% TS compared to $CaCO_3$ (6%), $MgSO_4$ (-2%) and the non-amended manure (6%). In the 45- to 75-cm layer, P removal decreased significantly and similarly for all amendments as initial TS concentration increased from 1% to 5%. Further increase in initial manure TS to 8% did not result in a significant net P removal for any of the amendments in this layer. In manure containing 5% and 8% TS, alum application resulted in a net accumulation of P in the 45- to 75-cm layer compared with the 51% P removal in manure containing 1% TS. Overall, amendments did not significantly improve P removal compared with the control treatment.

Table 3.5 Amendment type, manure initial solids content and settling depth effects on net P, N, Ca, Mg and K removal at the 24-h sampling time.

Effect	TP	TKN	Ca	Mg	K
			% net nutrient removal.		
Amendment					
Control	22	0.2	28	25	-1.40
$CaCO_3$	18	6.02	59	23	-2.97
$MgSO_4$	23	6.27	19	1.43	-2.56
Alum	24	-4.36	24	10	-1.20
Solids content (%)					
1	53	5.76	51	38	-0.85
5	3.97	1.76	24	0.83	-0.76
8	7.99	-1.43	23	6.08	-4.49
Depth (cm)					
30	27	7.04	42	17	-1.52
60	16	-2.98	24	13	-2.54
			P- value		
Solids content (S)	<0.001	0.71	0.01	0.001	0.01
Amendment (A)	0.6	0.61	<0.001	0.001	0.81
Depth (D)	0.02	0.16	0.02	0.01	0.32
S × D	0.001	0.03	<0.001	0.32	0.87
A × S	0.001	0.46	0.18	0.001	0.13
A × D	<0.001	0.29	0.02	1.00	0.001
A × S × D	0.01	0.85	0.03	0.96	0.03

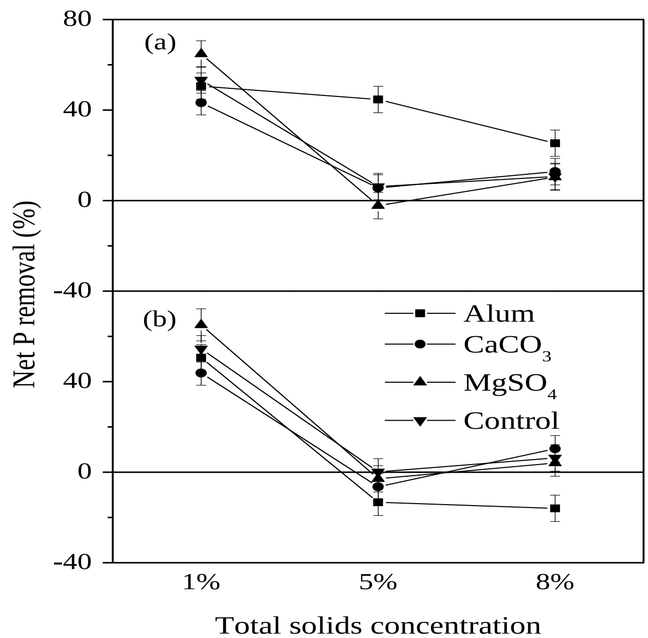

Figure 3.10 Net P removal in the 15- to 45- (a) and 45- to 75-cm (b) layers in liquid swine manure as affected by amendment type and initial manure total solids concentration after 24 h of settling.

3.7.11 Net Calcium, Magnesium and Potassium Removal After 24 h of Settling

Net Ca removal after 24 h of settling differed significantly ($P<0.0001$) among amendments; however, amendment differences varied with initial manure TS concentration and sampling depth, as indicated by the significant ($P = 0.03$) three-way interaction (Table 3.5). At all initial manure TS concentrations, $CaCO_3$ resulted in the greatest removal of Ca from the 15- to 45-cm layer (Fig. 3.11). Amendment differences were smaller in the 45- to 75-cm layer and, in this layer, Ca removal decreased sharply as initial TS concentration increased from 1% to 5%. Amendment differences in the layer were small, except for a significantly greater Ca removal from the $CaCO_3$ treatment compared with the alum treatment in manure containing 8% TS.

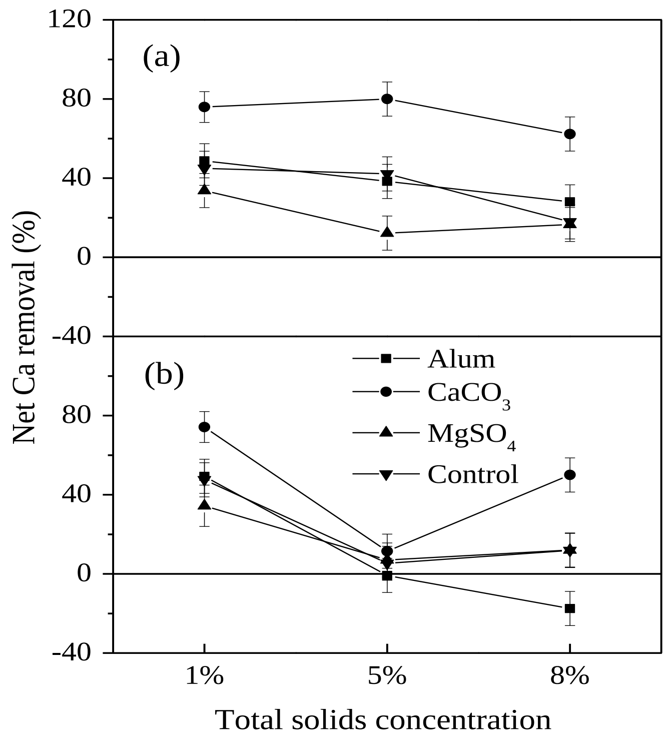

Figure 3.11 Net calcium (Ca) removal in liquid swine manure as affected by amendment type, initial total solids concentration of manure, and sampling depth.

Amendment effects on net Mg removal after 24 h of settling were significant ($P < 0.001$) but differences among amendments varied with initial TS concentration. (Table 3.5). Magnesium removal in alum-treated manure containing 1% TS and in the non-amended manure was higher than in $MgSO_4$-amended manure (Fig.3.12). For all initial manure solids concentrations, Mg removal was significantly higher in $CaCO_3$-treated than in $MgSO_4$-amended manure. As the initial solids concentration of the manure increased from 1% to 5%, Mg removal by alum and $MgSO_4$ decreased. Settling of manure also resulted in Mg removal in the non-amended manure with removal greater at 1% TS compared to both the 5% and 8% TS. In non-amended manure, 57% Mg was removed from manure containing 1% TS, which was higher than 35% Mg removed in alum-treated manure. Alum also improved Mg removal from manure, with a greater amount removed in manure containing 1% TS compared to the net accumulation of Mg observed at 8% TS.

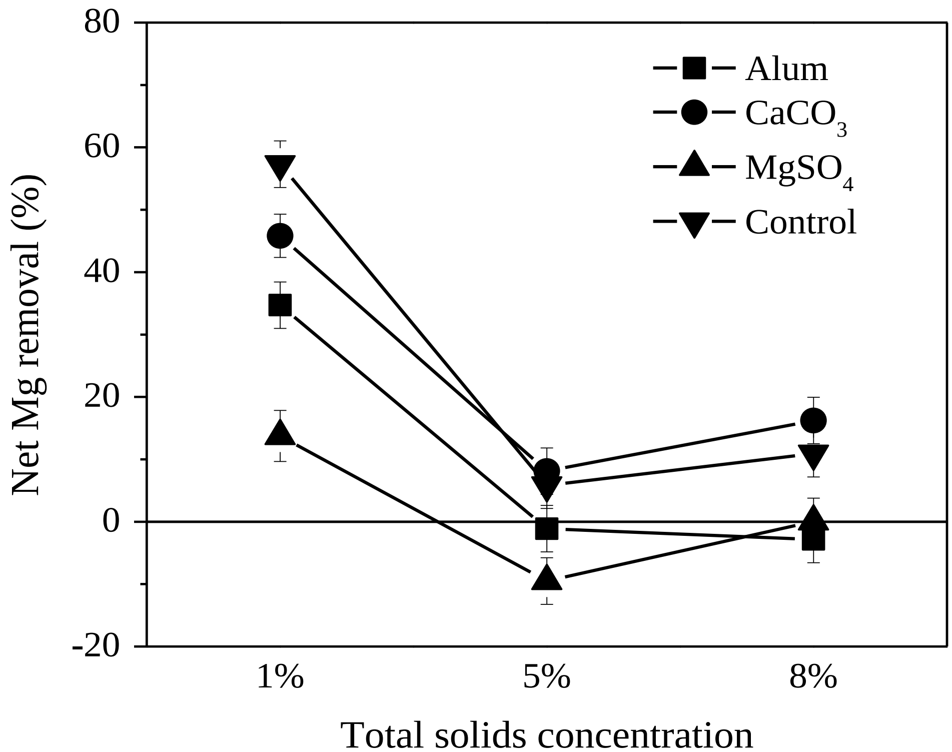

Figure 3.12 Net magnesium (Mg) removal in liquid swine manure as affected by amendment type and initial total solids concentration of manure.

Net K removal after 24 h of settling was not significantly affected by amendment type ($P = 0.81$). However, amendment differences varied with initial solids content (Table 3.5). Treatment of manure with $CaCO_3$ resulted in net K accumulation as manure initial TS concentration increased from 5% to 8% (Fig. 3.13).

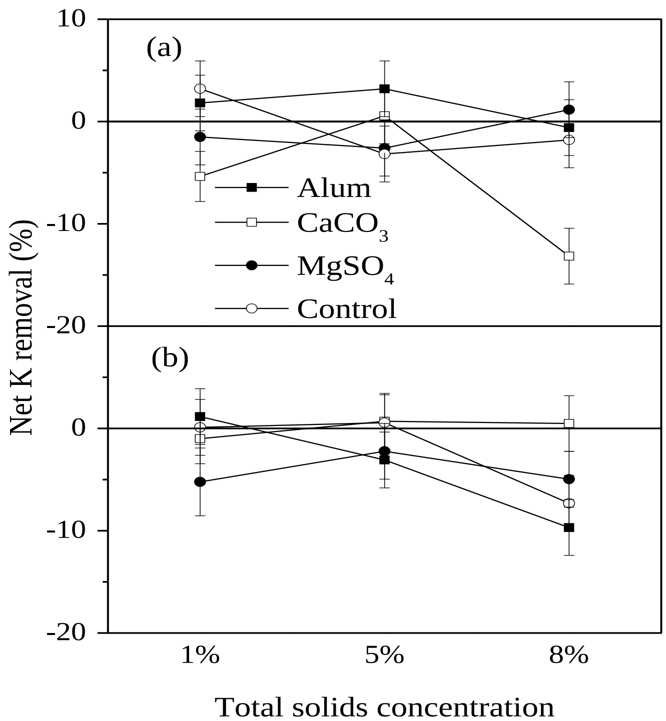

Figure 3.13 Net potassium (K) removal in liquid swine manure as affected by amendment type, initial total solids concentration of manure and sampling depth.

3.7.12 Net P, Ca, Mg and K removal at the 90 cm Depth and at 1% Initial Solids Concentration

There were no significant differences among amendments for P, Ca and Mg removal at the 90-cm depth in manure containing 1% initial TS concentration. However, there were significant temporal trends in the removal of these nutrients, which varied with amendment as indicated by the significant two-way interactions for P ($P < 0.001$), Ca ($P < 0.007$) and Mg ($P < 0.002$) at the 90-cm depth for manure containing 1% initial TS (Table 3.6). Alum resulted in an increase in P, Ca and Mg removal after 0.5 h of settling to peak at 4 h with only a slight increase after 8 h for P (Fig. 3.14) and Ca (Fig. 3.15) removal while it leveled off for Mg removal after 4 h (Fig. 3.16). This explains the significant amendment x time interaction for change in P, Ca and Mg removals. PAM effects on P, Ca and Mg removal were greater relative to alum at the 0.5 h sampling time, although not significantly different from the control. Alum increased P removal from 14% at 0.5 h to approximately 48% after 4 h. Similarly for Mg removal, alum treatment resulted in an increase in Mg removal from ~-1% at 0.5 h to approximately 35% after 4 h settling time. After 4 h, alum increased Ca removal from ~5% at 0.5 h to approximately 43% after 4 h.

Table 3.6 Amendment type and settling time effects on net P, N, Ca, Mg and K removal at the 90-cm depth in manure containing 1% initial solids concentration.

Effect	TP	TKN	Ca	Mg	K
	% Net nutrient removal.				
Amendment					
Control	47	12	36	49	1.50
Alum	42	-9.23	20	19	2.23
PAM	50	15	50	43	-4.23
Time (h)					
0.5	35	0.33	24	26	-0.23
1	40	-2.09	19	25	-1.36
2	47	2.02	31	35	-0.98
4	49	9.47	43	43	-0.95
8	51	9.56	46	44	1.01
24	52	15	49	46	1.51
			P value		
Amendment (A)	0.71	0.45	0.13	0.17	0.57
Time (T)	<0.001	0.58	0.01	0.003	0.64
A × T	<0.001	0.67	0.007	0.002	0.16

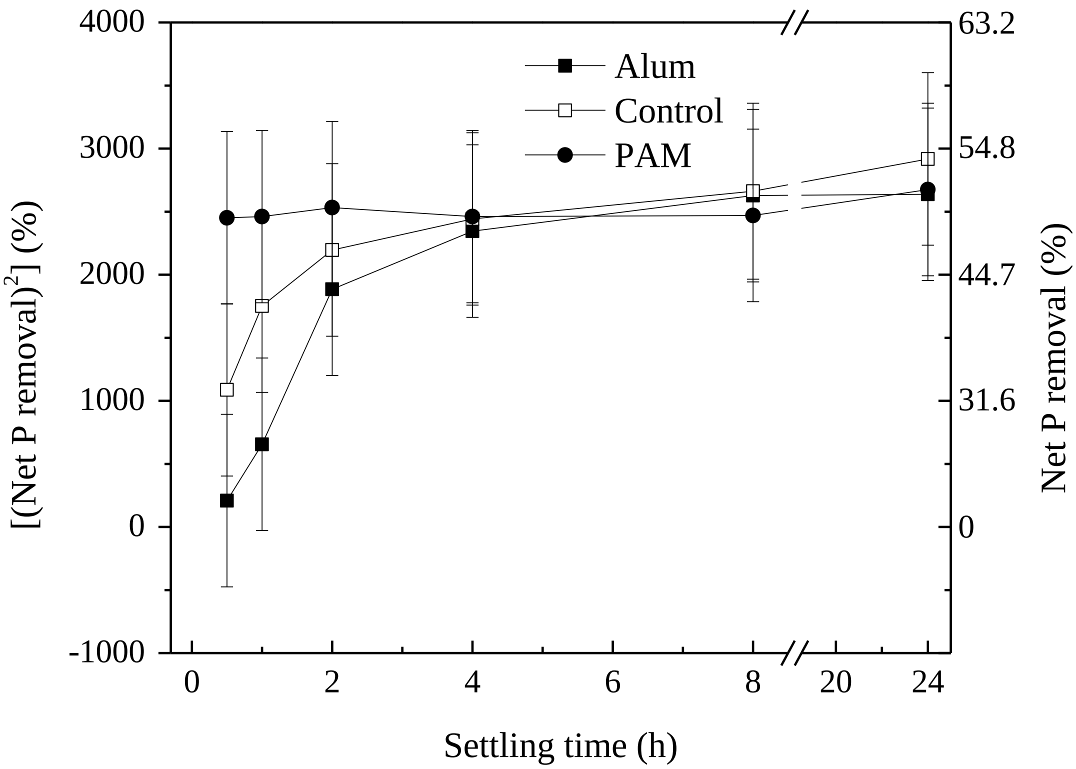

Figure 3.14 Amendment effects on net P removal at the 90-cm depth in manure containing 1% TS.

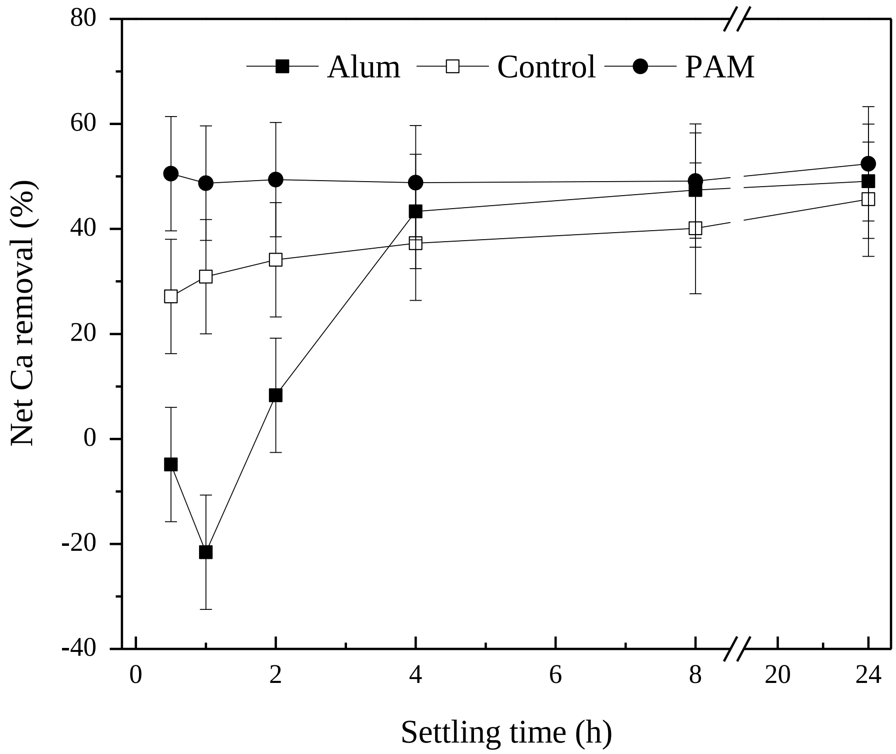

Figure 3.15 Amendment effects on net Ca removal at the 90-cm depth in manure containing 1% TS.

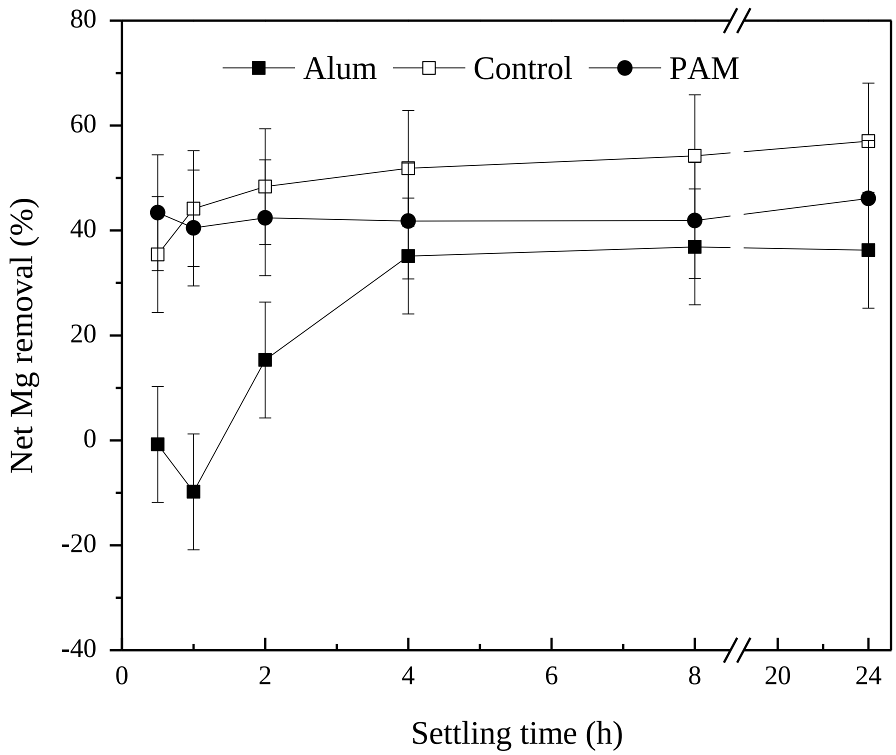

Figure 3.16 Amendment effects on net Mg removal at the 90-cm depth in manure containing 1% TS.

3.5 Discussion

3.5.1. Net Nutrient Removal

The fine suspended solids in liquid swine manure, which contain almost all the organic forms of nutrients, especially P and N, are often not separated by available mechanical separators (Hjorth et al., 2010; Vanotti and Hunt, 1999; Zhang and Lei, 1998). The use of chemical amendments (coagulants and flocculants) to remove nutrients involves three main processes: coagulation, flocculation, and precipitation of the aggregated flocs (Hjorth and Christensen, 2008; Hjorth et al., 2008). The addition of amendments such as alum, $CaCO_3$ and $MgSO_4$ to manure facilitates neutralization of the charge on the particle surface, which results in the destabilization of suspended solids, hence their aggregation (Hjorth and Christensen, 2008). These aggregated solids can then be easily removed by any mechanical separator method (Hjorth et al., 2010). Our results showed alum to be effective at removing P from the 15- to 45-cm layer in manure containing 1% TS but less effective at higher manure TS concentrations. The removal of P by alum in manure containing 1% TS after 4 h of settling from the 15- to 45-cm layer was approximately 52%, while alum treatment in manure containing 5% and 8% TS resulted in P removal of 17% and 1%, respectively. The improved P removal by alum at 1% TS may be a result of P precipitation and/or agglomeration of fine suspended solids (Christensen et al., 2009). Phosphorus removal from manure amended with alum, $CaCO_3$ and $MgSO_4$ significantly decreased as the solids concentration of manure increased from 1% through 5% to 8%. However, after 24 h of settling, alum seemed to remove more P from the 15- to 45-cm layer in manure containing 5% TS when compared with the other amendments. A similar pattern for P removal was observed in the non-amended manure, with a greater percentage of P removed in manure containing 1% TS than in manure with greater TS.

Our results for amendment effects on P removal are inconsistent with previous studies which showed much higher removal rates of P from swine manure. For example, while, in the present study, alum and PAM did not significantly improve P removal (~50% of P initially present in the manure) relative to the control in manure containing 1% TS, Power and Flatow (2002) reported 91% P removal in manure treated with 625 mg alum L^{-1} of manure. However, unlike in the present study, their study employed swine manure containing much lower TS (0.24%). Secondly, they utilized 1000 mL Imhoff settling cones, which, although commonly used for standard settling tests, are much smaller than the 21-L, 125-cm columns used in our study. The 125-cm depth in our study closely mimics manure settling tanks that would be used on swine operations. Thirdly, the application rate used for alum in our study (549 mg L^{-1}) was lower than that used in Power and Flatow's (2002) study, even though we used manure of higher TS (1% vs. 0.24%). Lastly, Power and Flatow (2002) used a settling time of 20 min whereas in the present study the settling experiment was 24 h in duration, even if much of the analysis focused on the first 4 h of settling.

Ndegwa et al. (2001) used large settling columns (91 cm high, 15 cm in diameter); settling times of 0.5, 1 and 4 h; drawout depths of 30 and 60 cm; and swine manure containing 1% TS, conditions which closely match those used in the present study. However, they applied 2.7 times more alum than used in our study. The greater alum dosage may explain the 78% P removal attained in their study, which was much greater than that measured in our study.

Differences between our results and those from other similar studies may also be due to differences in the characteristics of the swine manure and the mode of production in hog barns, which differ from one location to another and are largely affected by feed rations, growth stage of pigs, manure collection methods, and the quantity of water used in the manure collection system (Choudhary et al., 1996; Zhang and Westerman, 1997). The composition of swine manure varies depending upon the amount of water used on the pig farm. Characteristic parameters of swine manure, such as particle size distribution and initial total solids content, can significantly affect the removal efficiency of any solid-liquid separation technique (Hjorth et al., 2010; Zhu et al., 2000). Particle size distribution has a direct effect on the surface area available for flocculation and coagulation reactions (Christensen et al., 2009).

Our results showed that settling of swine manure solids following chemical treatment with alum and PAM, and in non-amended manure (control) was hindered and P removal reduced when initial manure TS concentration increased from 1% to 5 and 8%. This correlation between solids removal and P removal suggests that most of the P in the liquid swine manure is associated with the fine suspended solids (Christensen et al., 2009; Masse et al., 2005). Phosphorus removal due to PAM application is possibly due to its ability to destabilize and agglomerate the negatively charged organic suspended solids contained in the swine manure, thus forming settleable flocs (Garcia et al., 2007). Nonetheless, the effect of PAM was not significantly greater than that of the control treatment, except in manure containing 8% TS, in which P removal increased with time to higher levels than alum and the control, while there were no temporal trends associated with the latter two treatments. The PAM used in the present experiment has a moderate charge density and forms large aggregates through charge neutralization and bridging of organic suspended solid particles that contain most of the organic nutrients, especially P (Masse et al., 2010). Garcia et al. (2007) found that cationic PAM (Magnifloc 494 C) applied to a mixture of raw swine manure and P-rich sludge using working solutions of PAM at a rate of 60 mg L^{-1} active ingredient removed 83% P following screening (0.25 mm opening size). Vanotti and Hunt (1999), using sedimentation tests in a 1-L Imhoff cone, evaluated the effect of charge density of PAM on solids and nutrient removal from swine manure. They reported that 77% of organic P was removed from flushed swine manure treated with a 10 mg L^{-1} moderately charged, high-molecular weight cationic PAM (Magnifloc 494 C).

Addition of alum and PAM to manure containing varying TS concentrations did not increase the removal of N and K from swine manure. Nitrogen removal from swine manure was unaffected by alum, $CaCO_3$ and $MgSO_4$ following gravity settling. However, a small amount of N was removed by PAM (24%) in manure containing 5% TS, which was greater in the 15- to 45-cm layer compared to the 45- to 75-cm layer. Gravity settling of non-amended swine manure did not significantly affect N removal throughout the settling period. This suggests that most of the N and K are in the liquid fraction of the manure and are unaffected by coagulation and flocculation. Worley and Das (2000) also reported that N, Mg and K were unaffected by the addition of alum to flushed swine manure in a settling basin with a skimmer. In their study, approximately 20% of N and 8% of K were removed from the liquid swine manure before reintroduction into the lagoon. Converse and Karthikeyan (2004) reported a similar result for N removal from dairy manure allowed to settle for 4 h in 12-L settling columns (15-cm diameter). Natural sedimentation did not increase N removal from the dairy manure as settling time increased. In the present study, chemical treatment of manure with PAM and alum increased Mg and Ca removal from swine manure, with greater amounts removed in manure containing 1% TS compared with 5 and 8% TS. Application of PAM resulted in the removal of 50% Ca and 43% of Mg in manure containing 1% TS, while, with $CaCO_3$ application, similar proportions of Ca were removed from manure containing 1% TS (76%) and that containing 5% TS (80%) after 24 h of settling.

3.5.2 N:P ratio of Manure

Our results showed that settling of manure following chemical treatment did improve (increase) the N:P ratio of swine manure. The N:P ratio in the alum and PAM-amended manure from the 15- to 45- and 45- to 75-cm layers significantly increased after time 0 to peak at 9.1 after 1 h of settling in manure containing 1% TS. These results are consistent with studies that showed greater values for the N:P ratio following chemical addition. Walker et al. (2010) reported that the N:P ratio of liquid swine manure was improved from 3.6 to 17.1 in separated effluent in the first year, and 5.1 to 11.3 in the second year in manure treated with PAM before passing through a gravity belt thickener to remove the suspended solids. Vanotti et al. (2002) also reported that the N:P ratio of the liquid fraction increased from 5.1 to 11 after screening following flocculation. Their study investigated the use of PAM with swine manure of different initial TS concentrations for the purpose of improving the performance of screen separators. Vanotti et al. (2002) attributed the high N:P ratio to the greater P removal by PAM associated with the organic suspended solids, which are generally affected by flocculation coupled with mechanical separator. Worley and Das (2000) also reported that alum improved the N:P ratio of settling basin swine effluent from 3.6 without separation to 16.7 with alum addition. The lower ratios attained in our study reflect the low P removal efficiencies associated with the chemical amendments tested.

3.5.3 pH and Electrical Conductivity

Manure pH decreased as the initial TS concentration of liquid swine manure increased from 1% to 5% for all amendments. The pH of alum-treated manure containing 1% TS was below neutral (pH<7.0) and much lower (6.9) than that in non-amended and $CaCO_3$- and PAM-treated manure for most of the sampling period. The drop in pH following alum application was due to hydrolysis of Al, which increased the concentration of hydrogen ions in swine manure (Wang et al., 2005). Treatment of manure containing 1% TS with $MgSO_4$ also reduced the pH relative to PAM-amended manure, more so in manure containing 5% TS.

The pH of the liquid phase of manure is largely affected by the volatile fatty acids (VFA), NH_4^+ and HCO_3^- ions (Christensen et al., 2009). Manure pH is increased with the emission of CO_2 while emission of NH_3 results in a lower pH (Hjorth et al., 2010). Addition of alum to manure containing 5% TS resulted in a final pH of 5.7, which is within the optimum pH range (5.5-6.5) for P removal by alum (Wang et al., 2005). Manure pH affects P distribution between the liquid and solid fractions, with more P dissolved when pH is reduced (Hjorth et al., 2010).

Electrical conductivity (EC) was also affected by amendment treatment and initial TS of the swine manure. The EC was lower in the control, $CaCO_3$-, alum- and PAM-amended manure than in $MgSO_4$-amended manure. This is an indication that the concentration of ions in the liquid swine manure is high, which influences the flocculation of suspended solids that contain most of the P. Manure management methods used on the farm and the diets fed to the animals largely affect the composition of ions in animal manure (Hjorth et al., 2010). The most prevalent cations in swine manure are those of Ca, Mg, and Fe (Masse et al., 2005; Sommer et al., 2006) and EC depends on the concentration and speciation of these cations (Christensen et al., 2009; Hjorth et al., 2010).

3.6 Conclusions

Results from this study show that P removal (%) was greater in manure containing low TS concentration (1% TS) than in manure with higher TS (5% and 8%). In the non-amended manure, approximately 51% of P was removed with the solids fraction, during the first 4 h of settling, from the 15- to 45-cm layer in swine manure containing 1% TS, while 2% and 6% P were removed in manure containing 5% and 8% TS, respectively. Our results suggest that chemically-assisted sedimentation should be restricted to manure containing less than 5% TS and possibly not much greater than 1%. There was also limited evidence generated by this study to support the suggestion from previous studies that high amounts of nutrients, particularly P, are removed from swine manure when treated with either alum or PAM. Addition of alum to swine manure did not increase N and K removal from swine manure but PAM showed a slight increase in N removal and no effect on K removal. PAM removed approximately 50% of Ca from the 15- to 45-cm layer in manure containing 1% TS.

These results will assist swine producers in deciding on whether or which amendments to use as enhancers in different mechanical solids-liquid separation methods. There is still a need to examine some of the amendments used in the study, particularly alum and PAM, at higher rates comparable to those used in other previous studies.

3.7 References

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4. GENERAL SYNTHESIS

Manure management is a major issue in Manitoba because of the large quantity of manure generated annually by the hog industry. In order to protect the environment from excess nutrients, particularly P and N, proper management practices are required to minimize the adverse effects caused by the land-application of manure. Solid-liquid separation of manure is one of the many techniques commonly utilized to help manage the nutrients contained in swine manure (Zhu et al., 2004). Separating manure into both the P-rich solid and a N-rich liquid fraction offers the opportunity to manage the lost of P to the environment following land application of manure on agricultural fields (Christensen et al., 2009; Walker et al., 2010).

In this laboratory study, we obtained fundamental information on the effects of chemical amendments in enhancing settling of solids and nutrients from liquid swine manure of varying initial TS typical of hog operations in Manitoba, using gravity settling columns. Despite several attempts to understand solids and nutrient removal (especially P) in swine manure using various chemical amendments, the use of gravity settling columns that represent a typical on-farm settling tank on the field has not been adequately explored. Also, there is little information in Manitoba on solids and P removal from liquid swine manure by chemically-enhanced gravity settling. The main objective of this research study was accomplished in two parts. In the first part (Chapter 2), we evaluated solids removal from liquid swine manure as influenced by chemical amendments and initial TS of manure. The second part (Chapter 3) was focused on the extent of nutrient removal (especially P) with chemical amendments in manure of varying manure initial TS.

The results showed that chemical treatment increased solids removal compared with the non-amended manure. In particular, PAM removed more solids from manure containing 1% initial TS when compared with other amendments. This indicates that, if the goal in a hog barn is to separate liquid swine manure of initial TS around 1%, PAM will be the most appropriate amendment to use. However, if the main aim is to separate manure of higher initial TS greater 1% using gravity settling, the use of PAM should be avoided because of the re-suspension of the separated solids to the surface. Even if PAM were used, the settling should be terminated after 4 h and the liquid pumped out from the settling tank.

Results from the study indicate that greater extent of solids removal by PAM did not translate into greater P removal from the liquid swine manure. This suggests that while PAM is an effective amendment for separation of solids from liquid swine manure, it has limited effectiveness in removing P from the liquid fraction of swine manure. Land application of the resulting liquid fraction within the immediate vicinity of the hog barn might result in P-loading.

The coagulation and flocculation of solids and P associated with the fine suspended solids could conceivably be improved by the use of chemical mixtures such as alum plus PAM. Although alum was not as effective as PAM in separating the solids, our results showed that as the initial TS of manure was increased from 1% to 5% and 8%, P removal from the 15- to 45-cm layer of alum-treated manure after 24 h of settling remained fairly stable compared with the other amendments that showed a sharp decline in P removal. The implication is that alum might be the most appropriate amendment to separate P if the manure initial TS on a hog barn is greater than 5%. Our results also showed that the rate of P removal in the non-amended manure increased with time, with a greater amount of P removed after 24 h of settling in manure containing 1% TS. This indicates that gravitational settling without chemical amendment has the potential to improve P removal from swine manure. However, the use of natural sedimentation in settling tanks on farms may take a longer time for all the P associated with the fine suspended solids to settle out compared with manure amended with PAM.

4.1 Future Work

It is likely that rates of alum and PAM used in this study, especially at high manure TS, were below those required for effective solids and P removal. Further research is needed to investigate solids and P removal from liquid swine manure of varying initial TS concentration at higher amendment rates comparable to those used in other previous studies. This could possibly enhance solids aggregation and the eventual removal of P from swine manure following chemical treatment. Amendment rates used in the experiment were based on previous studies and linearly extrapolated for manure of higher (5% and 8%) initial TS concentration. We recommend that determination of the optimum dosage of the amendment used in the study, particularly PAM and alum should be carried out at each individual initial TS concentration instead of using linear extrapolation of rates determined at lower initial TS. More importantly, the effectiveness of these amendments should be evaluated using liquid swine manure containing ~3%

initial TS typical of most finisher barn operations (phytase use) in Manitoba. Also, because of the resuspension of solids occurring at settling time beyond 4 h at higher initial TS concentration (that is 5% and 8%), there is a need to identify the TS concentration of manure above which PAM will be ineffective. Since 75% of the total P contained in liquid swine manure is inorganic, there is likely some merit in testing the effectiveness of amendment mixtures, e.g., the use of alum in combination with PAM, or the use of amendments in conjunction with mechanical treatment technologies. Application of PAM will aid the agglomeration of the suspended particles into settleable flocs, while alum will result in the precipitation of the inorganic P leading to increased P removal (Zhang and Lei, 1998). There is also a need to further examine the forms of P in manure and in separated solids so that P removal can be described in terms of the proportion of each manure fraction removed.

4.2 References

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5. APPENDICES

Appendix A: Supplementary graphs

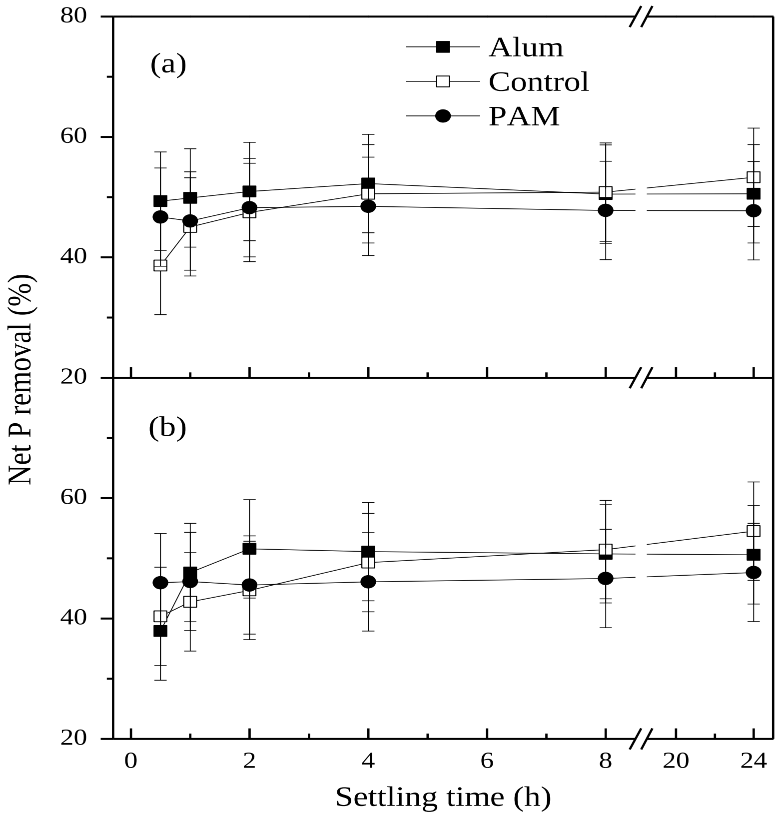

Figure A.1 Amendment effects on net P removal in the 15-to 45- (a) and 45- to 75-cm (b) layers in manure containing 1% TS.

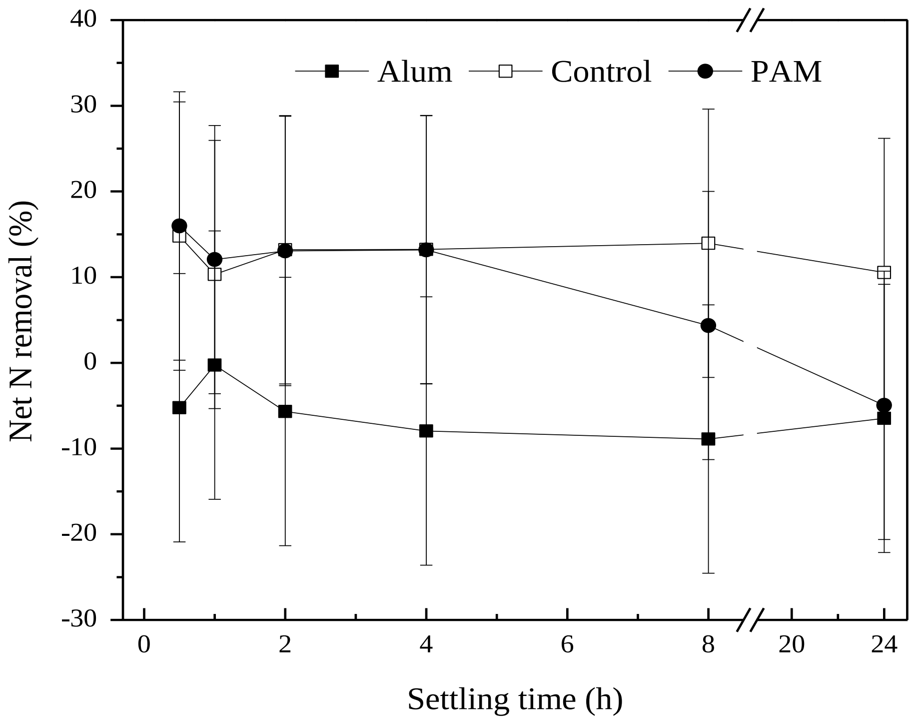

Figure A.2 Amendment effects on net N averaged from the 15- to 45- and 45- to 75-cm layers in manure containing 1% TS.

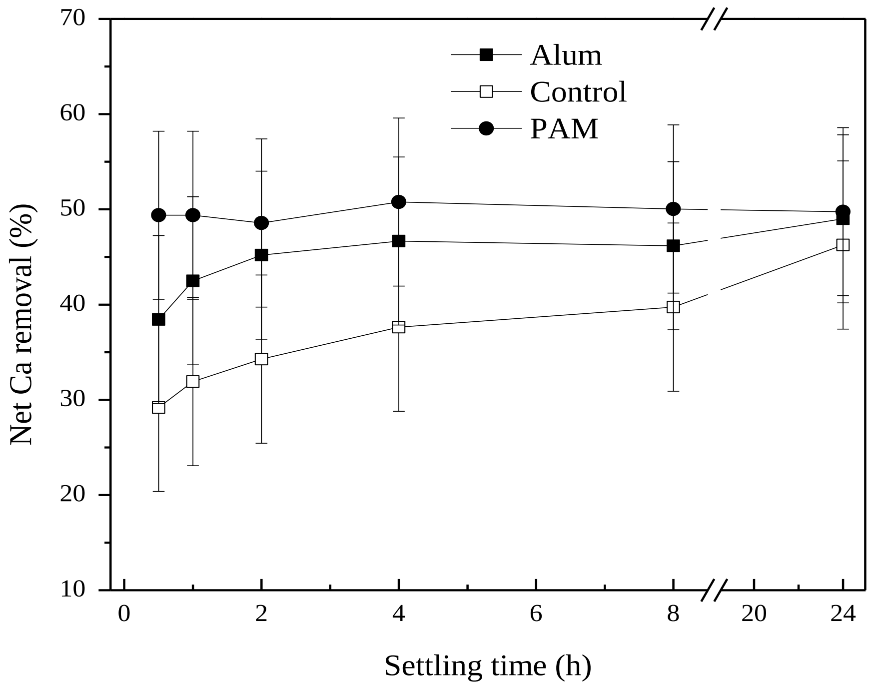

Figure A.3 Amendment effects on net Ca removal averaged from the 15- to 45- and 45- to 75-cm layers in manure containing 1% TS.

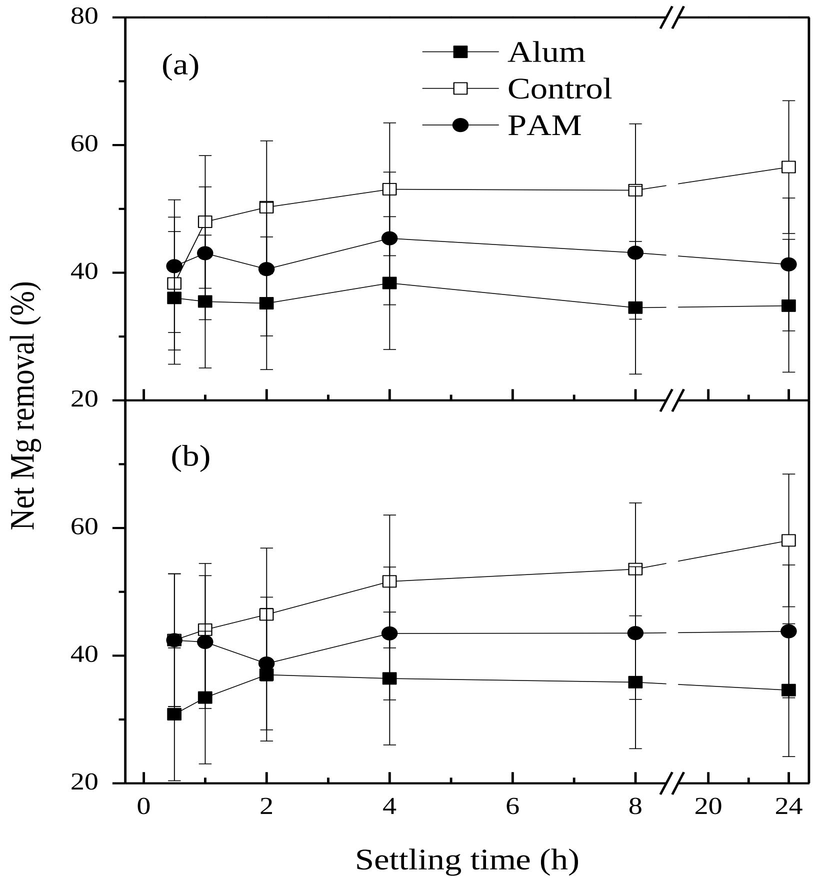

Figure A.4 Amendment effects on net Mg removal in the 15- to 45- (a) and 45- to 75- cm (b) layers in manure containing 1% TS.

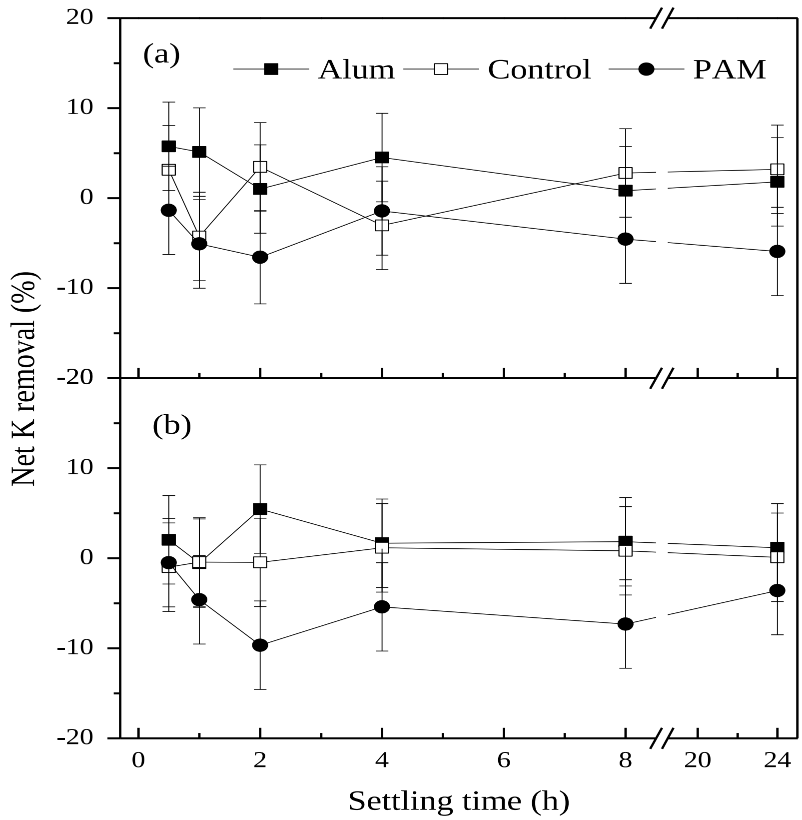

Figure A.5 Amendment effects on net K removal in the 15- to 45- (a) and 45- to 75-cm layers in manure containing 1% TS.

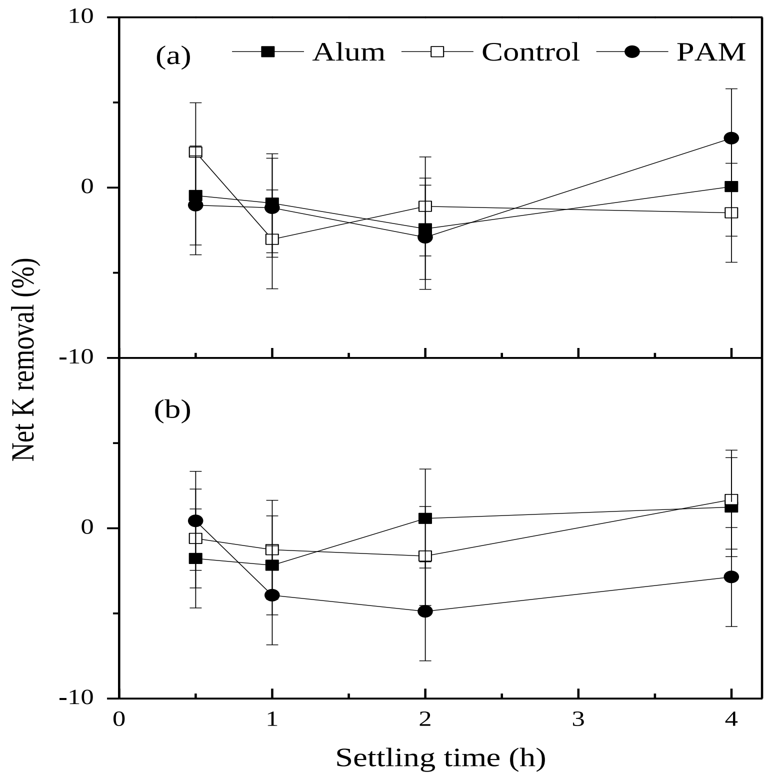

Figure A.6 Amendment effects on net K removal in the 15- to 45- (a) and 45- to 75-cm layers in manure averaged across initial TS concentrations.