



# Phosphorus recovery from pig manure solids prior to land application



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## ABSTRACT

Land disposal of pig manure is an environmental concern due to an imbalance of the nitrogen to phosphorus (N:P) ratio for crop production, leading to excess phosphorus (P) in soils and potential risks of water pollution. A process called “quick wash” was investigated for its feasibility to extract and recover P from pig manure solids. This process consists of selective dissolution of P from solid manure into a liquid extract using mineral or organic acid solutions, and recovery of P from the liquid extract by adding lime and an organic polymer to form a P precipitate. Laboratory tests confirmed the quick wash process selectively removed and recovered up to 90% of the total (TP) from fresh pig manure solids while leaving significant amounts of nitrogen (N) in the washed manure residue. As a result of manure P extraction, the washed solid residue became environmentally safer for land application with a more balanced N:P ratio for crop production. The recovered P can be recycled and used as fertilizer for crop production while minimizing manure P losses into the environment.

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## 1. Introduction

Land application of large amounts of manure generated by animal feeding operations is an environmental concern often associated with excess P in soils and potential risks of water pollution. Because of a disproportion of N and P contents in pig manure and harvested crops, repeated applications at optimal N rates for crop growth result in accumulation of P in soils. For instance, the average N:P ratio in plant biomass of most grain and hay crops is 8:1, whereas animal manure has a smaller N:P ratio (<4:1) (Zhang et al., 2003). Due to this nutrient imbalance, eutrophication of rivers and lakes can be accelerated as excess soil P is lost to aquatic environments through soil leaching and runoff (Vitousek et al., 2009; MacDonald et al., 2011). To reduce adverse effects of manure P losses into the environment, a substantial amount of P needs to be moved off the pig farm by transporting manure to P-deficit croplands (NRCS, 2003). However, transportation of pig manure in bulk becomes less cost and energy-effective with increasing distance from manure production sites (Keplinger and Hauck, 2006). Ideally, manure management in concentrated livestock regions could include new technologies for the recovery of manure P in a concentrated, usable form. This approach would make more economical the long distance transfers of manure P while reducing

both agronomic P imbalances and adverse effects of soil P losses on water resources.

A number of physical, chemical, and biologic processes have been identified as potentially useful for the recovery P from animal manure and biosolids (Szögi and Vanotti, 2009; Vaccari, 2011). In particular, there is much interest on P recovery from solid animal manure by wet extraction of P from the byproducts of thermal treatment. In the thermal treatment approach, the organic matter is destroyed through incineration, pyrolysis, gasification, or liquefaction, and the phosphorus is extracted from the residue. For instance, P was recovered in a two-step precipitation process from chicken manure incineration ash extracted with a 1.0 M hydrochloric acid solution. Heavy metals impurities were first precipitated at pH 3.05 using sodium hydroxide and removed by filtration. Phosphorus was then recovered by raising the pH of the filtrate to 8.2 forming a precipitate containing 92% of its P as calcium phosphate (Kaikake et al., 2009). Another thermal method for conversion of biomass is pyrolysis, which produces a combination of gas, liquid fuel, and charcoal also known as biochar (Cantrell et al., 2008). Following pyrolysis of manure, P can be recovered from the biochar after wet extraction using mineral acids. For instance, about 92%–97% of the P present in fresh manure was recovered in the biochar fraction, much of which (60%–75%) was extracted as inorganic P using a 0.2 M sulfuric acid solution (Azuara et al., 2013). Thermal conversion processes such as incineration and pyrolysis require a relatively dry feedstock such as poultry litter or beef feed lot manure (Cantrell et al., 2008). Other thermal processes such as

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wet pyrolysis and supercritical water gasification can use wet feed stocks such as liquid animal manure, and recover P from their char products by precipitation after acid extraction (Libra et al., 2011; Yanagida et al., 2009). These thermal conversion methods can provide byproducts rich in recoverable P but partial or total loss of N during thermal conversion make them less attractive for use as balanced N and P sources for crop production.

As an alternative to improve the N and P balance in manure byproducts, a new treatment process called “quick wash” was developed for rapid wet extraction of P from raw solid manure and recovery of manure P in solid concentrated form (Szögi et al., 2014). This process consists of selectively extracting P from solid manure using mineral or organic acid solutions, and recovery of P from the extract by adding lime and an organic polymer forming a calcium-containing P precipitate. The quick wash process has three products: 1) a washed solid with a N:P ratio optimal for use in crop production; 2) a concentrated solid P material that can be transported long distance and used as an effective P fertilizer; 3) a liquid effluent that could be applied to nearby cropland as liquid fertilizer or recycled into the treatment system. Compared with thermal methods described above, the quick wash process avoids loss of oxidizable organic C and N from treated manure because it is conducted at ambient temperature. Therefore, the washed manure would be more environmentally safe for land application given that its N:P ratio is better balanced to match specific crop needs. In addition, the recovered P product could be transported to P-deficient croplands for use as a plant fertilizer. The objectives of this paper were to gain new insights into this new treatment process, and to evaluate its technical feasibility for improving pig manure N:P ratio prior to land application while reducing the potential P losses into the environment.

## 2. Materials and methods

### 2.1. Basic process configuration

The basic quick wash process includes three steps (Szögi et al., 2014): (1) selective P extraction, (2) P recovery, and (3) P recovery enhancement (Fig. 1). In the first step, manure solids are mixed with an acidic solution to form a washed solid residue (with a higher N:P ratio than the untreated manure solids) and a liquid P extract. In step 2, P is precipitated under alkaline conditions by adding lime to the liquid extract, and in the final step (step 3) the addition of an organic anionic polymer, polyacrylamide (PAM), enhances the formation and recovery of a calcium-containing P precipitate.

**Table 1**

Rates of acids applied to manure solids for extraction of P in step 1 of the quick wash process.

Treatment	Acid rate (mmol L <sup>-1</sup> )	Citric (g L <sup>-1</sup> )	HCl <sup>a</sup>
0	0	0	0
1	2.5	0.48	0.24
2	5	0.96	0.49
3	10	1.92	0.98
4	20	3.84	1.96
5	40	7.69	3.92
6	80	15.37	7.84

<sup>a</sup> 37.2% HCl with specific gravity 1.19 at 15 °C.

### 2.2. Experimental

The feasibility of applying the quick wash process to pig manure was evaluated by performing the following two sets of experiments: 1) selective extraction of P from pig manure solids using either organic (citric) or mineral (hydrochloric) acids; and 2) P precipitation and recovery by precipitation under alkaline pH without and with precipitation enhancement by anionic PAM addition.

For the first experiments, pig manure was collected from a farrow to finish farm in Florence Co., SC that housed 280 heads in a barn that used an open gutter and flushing system to handle the manure. A composite fresh manure sample was collected from the inclined gutter between flushes using a shovel and placed in a 20-L plastic container, transported on ice to the laboratory, and stored at 4 °C until analysis. The manure sample had a fresh weight content of 8.1 g TN kg<sup>-1</sup>, and 3.9 g TP kg<sup>-1</sup> with 78.7% moisture, or 37.8 g TN kg<sup>-1</sup>, and 18.2 g TP kg<sup>-1</sup> on dry weight basis, and an equivalent dry weight P<sub>2</sub>O<sub>5</sub> content of 4.2%. For the second set of experiments, manure was obtained from a barn with a flush system under a slatted floor at the Pig Unit, North Carolina State University, Lake Wheeler Road Field Laboratory, Raleigh, NC. To obtain the pig manure solids, the flushes were held for 24 h to allow manure solids accumulate under the slatted floor. Again, manure solids were collected with a shovel, placed in a plastic container, transported on ice to the laboratory, and placed in cold storage until the start of the experiment. This second manure sample had fresh weight contents of 9.9 g TN kg<sup>-1</sup>, and 7.1 g TP kg<sup>-1</sup>, with 70% moisture, or 33.1 g TN kg<sup>-1</sup>, and 23.7 g TP kg<sup>-1</sup> on dry weight basis, and an equivalent dry weight P<sub>2</sub>O<sub>5</sub> content of 5.4%.

#### 2.2.1. First experiment: selective P extraction

Citric and hydrochloric (HCl) acids were tested for their ability to selectively remove P. Each acid was applied at six concentration levels (2.5, 5, 10, 20, 40, and 80 mmol L<sup>-1</sup>) plus one treatment

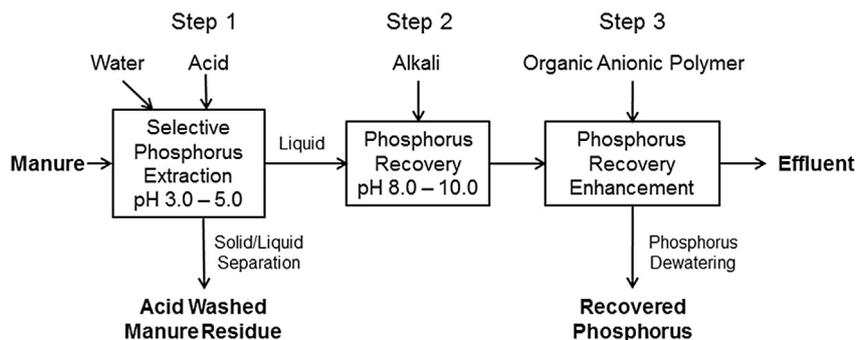


Fig. 1. Quick wash process schematic.

control (treatment 0) using only water (Table 1).

Solutions of citric acid were added to a set of 2.00 g manure solids samples in 50 mL graduated glass test tubes (1:25 w/v ratio). In a similar manner, solutions of HCl were added to another set of 2.00 g manure solids samples. The acid solutions and manure solids were mixed in a reciprocating shaker (135 oscillations  $\text{min}^{-1}$ ) at ambient temperature (23 °C) and pressure (101.3 kPa) for 1 h. Subsequently, solids and liquid were separated by centrifugation at 2000 g for 5 min. The liquid supernatant was decanted and analyzed for pH, TP, and total Kjeldahl N (TKN). Washed solids were dried at 40 °C in a forced-air drier and analyzed for TKN and TP. The extraction experiment was conducted in duplicate, and the treatment control consisted of extraction with distilled water. Phosphorus extraction efficiencies of the two acid treatments were established by comparison of P extraction relative to initial P content in untreated pig manure.

### 2.2.2. Second experiment: phosphorus precipitation and recovery

A 64-g pig manure sample was mixed (1:25 w/v) with 1.6 L of a 10  $\text{mmol L}^{-1}$  citric acid solution in a 2-L beaker and stirred for 1 h with a magnetic stirrer. The citric acid concentration level was selected based on the results of experiment 1. After settling for 20 min, the liquid extract was separated from the washed solid residue by decantation and transferred in 35-mL aliquots to separate laboratory vessels (50-mL graduated glass tubes). A 2% (w/v) hydrated lime [ $\text{Ca}(\text{OH})_2$ ] solution in water was added in various amounts until the pH of the mixed liquid reached set points of 6, 7, 8, 9, 10, and 11 units. A control treatment with no lime addition was included (pH 4.5). While half of the vessels only received lime treatments (Step 2), the other half received the lime treatments plus a dose of anionic polymer (Step 3). The anionic polymer was a PAM with 34% mole charge (Magnafloc 120L, Basf Corp., Suffolk, VA) and 50% active ingredient (a.i.). The anionic PAM was added to all six lime treatments at a single rate of 7.0  $\text{mg a.i. L}^{-1}$  and mixed for 30 s to enhance the recovery of P (Szögi et al., 2006a). For both lime only and lime plus anionic polymer tests, the liquid supernatant was decanted and analyzed for pH, TP, and TKN. Solids were dried at 40 °C in a forced-air drier and analyzed for TKN and TP. The P precipitates were rinsed three times with distilled water and recovered by filtration with glass microfiber filters (Whatman 934AH, Whatman, Inc., Clifton, N.J.). The P precipitates were dried at 40 °C in a forced-air drier, weighed to determine the amount of solid material produced, and analyzed for TKN and TP.

### 2.3. Analytical methods

Analyses of liquid and solids were performed according to Standard Methods for Examination of Water and Wastewater (APHA, 1998). Total P and TKN were determined by colorimetric methods using the automated ascorbic acid method (Standard Method 4500-P F) and the phenate method (Standard Method 4500-NH<sub>3</sub> G), respectively, adapted to digested extracts using sulfuric acid (Pote and Daniel, 2000). Total ammoniacal N (TAN) was determined by the automated phenate method in undigested samples. Total N is the sum of TKN plus nitrate-N. Nitrate-N was determined using Standard Method 4500-NO<sub>3</sub><sup>-</sup> F in undigested samples but it represented less than 2% of TN in all analyzed samples. After filtration of liquid samples through a 0.45- $\mu\text{m}$  membrane filter (Gelman Supor-450; Pall Corp.), soluble reactive P (RP) and soluble TP were determined in undigested and digested samples, respectively, using the automated ascorbic acid method. The pH of liquid samples was measured electrometrically using a combination pH electrode (Standard Method 4500-H<sup>+</sup> B). Total suspended solids (TSS) were determined by retaining solids on a glass-fiber filter (Whatman grade 934AH, Whatman, Inc., Clifton,

N.J.) and drying to 105 °C (Standard Method 2540 D). Data analyses were performed using the General Linear Model procedure in SAS statistical software (SAS Institute, 2011). Statistical results included means, standard deviations, analysis of variance (ANOVA), and least significant difference at a 0.05 probability level ( $\text{LSD}_{0.05}$ ) for multiple comparisons among means.

### 2.4. Phosphorus treatment efficiency and mass flow balance

Process efficiencies of the various treatments (acid type and rates, hydrated lime rates and anionic polymer) were expressed as percentage of P extraction or recovery relative to initial P content. The N and P flow throughout the quick wash process was estimated using a mass flow balance (Szögi and Vanotti, 2014). The mass flow balance included the TN and TP mass input and outputs from each step of the process as a percent of the initial content of N and P in untreated manure.

## 3. Results and discussion

### 3.1. Phosphorus extraction

In step 1 of the quick wash, P was extracted from pig manure solids at increasing molar concentrations (0–80  $\text{mmol L}^{-1}$ ) of both citric and HCl acids (Table 2). During acid extraction, a significant portion of total P in pig manure solids was hydrolyzed and transferred into the extract solution. Total P extraction rates increased with increasing acid concentrations. With citric acid, acidic pH values in the range of 4.7 to 3.2 units were obtained with applications of 5–20  $\text{mmol L}^{-1}$ . These citric acid application rates provided removal rates of 82–90% of the initial TP, respectively (Table 2). In contrast, the control with distilled water extracted only 49% of the initial TP in manure solids. In addition to the concentration of acid, the type of acid (citric vs. HCl) made a difference. At similar molar concentrations, citric acid was more efficient at extracting P than HCl. For instance, the citric acid at 10  $\text{mmol L}^{-1}$  extracted 87% of the initial TP content in manure solids whereas HCl at the same concentration only extracted 75% of the initial TP. At increasing concentrations beyond 20  $\text{mmol L}^{-1}$ , more intense acidification (pH < 3.0) was obtained with HCl than with citric acid. High P extraction efficiencies similar to citric acid (88%) were also reached with HCl using twice the molar concentration (40  $\text{mmol L}^{-1}$ ) with a corresponding extraction pH of 1.8 (Table 2). At this low pH, the extracting liquid becomes corrosive, and unnecessary oxidation of organic compounds can occur. From these results, we concluded that use of an organic acid was a more rate effective and less corrosive option for use in a quick wash treatment system at real scale.

### 3.2. Washed solids residue – N:P ratio

While P extraction increased with increasing concentrations of citric or HCl acid (49–91%), TN contained in manure solids was extracted much less efficiently (37–49%) than P (Table 2). In a previous study of the quick wash process using on poultry litter (Szögi et al., 2008), similar higher extraction efficiencies of TP versus TN were observed when several organic and inorganic acids were used to extract P at pH < 5.0. Accordingly, the quick wash P extraction is considered selective with respect to N because a significant fraction of N remains in the washed solid residue while most P is extracted as shown in Table 2. As a result of the selective P extraction, the acid washed manure residue has a significantly higher N:P ratio than the untreated manure solids (N:P = 2.1) or the control washed with distilled water (N:P = 2.8, Table 2). For instance, 87% of initial total P in manure was extracted in citric acid

**Table 2**  
Acid treatment effect of citric and hydrochloric acids on extraction of N and P from pig manure solids, step 1 of the quick wash process.

Treatment	Acid rate (mmol L <sup>-1</sup> )	Extraction pH <sup>a</sup>	Extracted in liquid supernatant				TP remaining in washed solids (g kg <sup>-1</sup> )	P Mass accounted <sup>d</sup> (%)	N:P ratio washed manure solids <sup>e</sup>
			TN <sup>b</sup>		TP <sup>c</sup>				
Citric			(g kg <sup>-1</sup> )	(%)	(g kg <sup>-1</sup> )	(%)			
0	0	6.9	3.5	43	1.9	49	2.0	100	2.8
1	2.5	5.4	4.0	49	2.7	69	1.2	100	5.6
2	5	4.7	3.6	44	3.2	82	0.6	98	10.9
3	10	3.8	3.2	40	3.4	87	0.7	104	11.5
4	20	3.2	3.0	37	3.5	90	0.7	107	9.2
5	40	2.8	3.4	42	3.5	90	0.7	108	8.7
6	80	2.5	3.5	43	3.5	90	0.9	112	7.3
<b>HCl</b>									
0	0	7.0	3.7	44	2.1	51	1.9	100	2.8
1	2.5	5.9	3.2	40	2.2	57	1.5	95	3.6
2	5	5.5	3.2	40	2.5	65	1.3	97	4.8
3	10	4.5	2.9	36	2.9	75	0.9	97	7.4
4	20	2.5	2.4	30	3.0	76	0.9	100	8.5
5	40	1.8	3.0	37	3.4	88	0.7	105	8.5
6	80	1.4	3.8	47	3.5	91	0.5	103	9.0
LSD <sub>0.05</sub> <sup>f</sup>		0.2	0.5	6	0.1	4	0.3		1.2

<sup>a</sup> Data are means of two replicates.

<sup>b</sup> TN extracted = TN extraction relative to initial TN content in fresh manure (8.1 g N kg<sup>-1</sup> wet weight, 78.7% moisture).

<sup>c</sup> TP extracted = P extraction relative to initial P content in fresh manure (3.9 g P kg<sup>-1</sup> wet weight, 78.7% moisture).

<sup>d</sup> P mass accounted = ((TP remaining in washed solids + TP extracted)/initial P content in fresh manure) × 100.

<sup>e</sup> Untreated manure solids N:P ratio = 2.1.

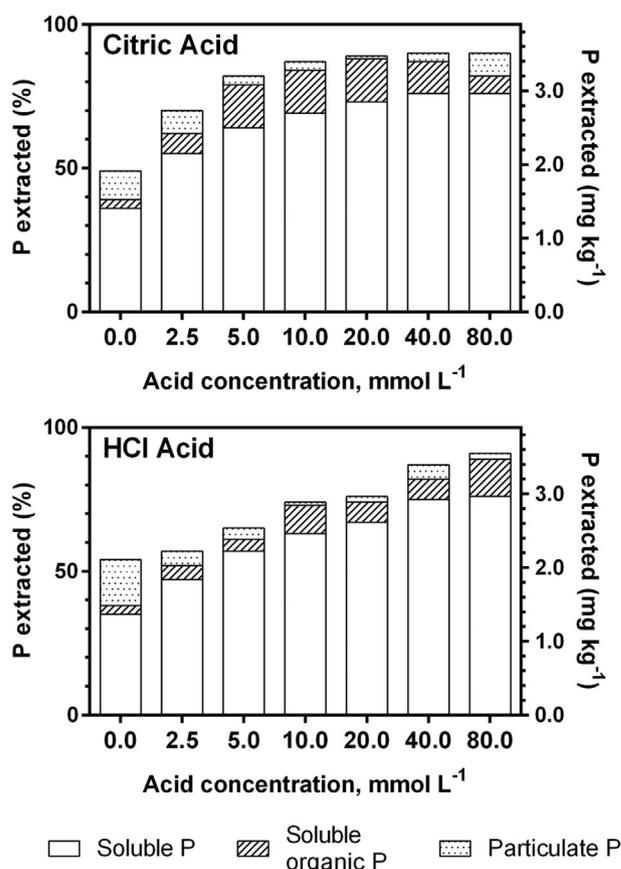
<sup>f</sup> Least square difference (LSD) value is for comparison of any two means within the same column.

treatment 3 at 10-mmol L<sup>-1</sup> of citric acid (pH 3.8) whereas only 40% of initial TN at the same acid rate (Table 2). The washed residue from this treatment ended with a N:P ratio of 11.5 (Table 2). This N:P ratio was 5.4-fold higher than the N:P ratio of the untreated pig manure (N:P = 2.1), and is within the N:P ratio range of 3.3–16.7 for balanced fertilization required by typical crops and pastures (Szögi and Vanotti, 2009; Zhang et al., 2003). Therefore, the quick wash process reduces agronomic P imbalances of the manure leaving significant amounts of N in the washed manure residue with a more favorable N:P ratio for crop production, and making the washed manure solids environmentally safe for land application on a N basis.

### 3.3. Soluble phosphorus in acid extracts

The amount and form of P in fresh manure varies greatly depending on the age, class, nutrient status of the pig, P and other nutrient content of the feed, and inorganic P supplements added to the feed (National Research Council, 1998). Fresh pig manure usually contains 60–70% as total inorganic P and 30–40% as organic P (Havlin et al., 1999). Other studies reported pig manure extracted with 1.0 M HCl released inorganic P by dissolution of Ca, Mg and Al phosphates while release of organic P was simultaneously accomplished by hydrolysis of phytate and monoester-P compounds (Ajiboye et al., 2007; Pagliari and Laboski, 2012). In order to estimate how much inorganic and organic P was soluble in step 1 of the quick wash, we determined the soluble TP and reactive P (RP) fraction in the acid extract; the soluble unreactive (UP) fraction was estimated by difference between soluble TP and RP. However, when P is determined using colorimetric analysis methods, the UP contains organic forms plus some condensed forms of P (such as polyphosphates) while the RP includes inorganic P as well as loosely bound organic forms released by acid hydrolysis (Haygarth and Edwards, 2000). Since in our study P was determined by colorimetric analysis, the RP and UP fractions were assumed as rough estimates of soluble inorganic and organic P fractions, respectively. Therefore, the acid treatments in our study effectively solubilized a large fraction of inorganic P-containing compounds. Both citric and HCl acid treatments extracted 63–76% of the fresh manure TP as RP

within the acid application rates of 10–80 mmol L<sup>-1</sup> (Fig. 2). These acid treatments also hydrolyzed organic phosphates; citric acid released as much as 15% of the manure TP as UP at a rate of 10 mmol L<sup>-1</sup> whereas HCl released as much as 13% as UP at the



**Fig. 2.** Percent soluble reactive P (RP) and soluble unreactive P (UP) extracted with respect to initial TP (3.9 g kg<sup>-1</sup>) in fresh manure solids at increasing rates of citric and HCl acids.

highest application rate of 80 mmol L<sup>-1</sup> (Fig. 2). Our results indicate that RP contribution to the extract is very important because it could constitute a major fraction of the recovered P material in step 3 of the quick wash process in the form of inorganic P.

#### 3.4. Phosphorus precipitation and recovery enhancement

After separating the acid liquid P extract from the washed solid residue, we evaluated the recovery of P from the acid extract (Fig. 1). In step 2, soluble P in the liquid extract was precipitated by addition of hydrated lime (2% w/v) to form calcium–P compounds. In step 3, anionic polymer was added to enhance recovery and P concentration of the precipitated product. After liquid–solid separation by decantation, the extract solution (10 mmol L<sup>-1</sup> citric acid) obtained in step 1 of the quick wash had a pH 4.5 and a TP concentration of 256 mg L<sup>-1</sup> with no lime addition. As shown in Table 3, TP concentrations decreased significantly in the liquid extract with increasing lime application rates (step 2). The percent removal of TP from the liquid extract at any lime rate in step 2 was significant with respect to the control (no lime), however, at the highest pH of 11.0 (3.1 g L<sup>-1</sup> lime) only 51% of the TP was removed from the liquid extract with no polymer addition (Table 3).

In step 3, the P precipitation was significantly enhanced by adding to all lime treatments a single rate of 7 mg L<sup>-1</sup> of anionic polymer (Table 3). With anionic polymer addition, a pH increase in between 8.0 and 9.0 units was sufficient to remove and precipitate 96–99% of the TP from the acid liquid extract. The significant enhancement of TP recovery in the precipitate with respect to the initial content of P in fresh pig manure is summarized in Fig. 3.

From the TP analysis of the recovered precipitate, it was found that as much as 90% of initial TP in pig manure solids can be recovered in the third step of the quick wash process (Table 4). On a dry weight basis, the highest P<sub>2</sub>O<sub>5</sub> content of the recovered P precipitate was 12.8% (obtained at pH 8), which was 2.4-fold more concentrated than the initial content of 5.4% P<sub>2</sub>O<sub>5</sub> of untreated pig manure solids.

After recovering the P precipitate, the remaining liquid contained N but very little P (Table 5). A significant fraction of TN was in organic N form which was determined as the difference between TKN and TAN. For instance, the effluent obtained at pH 8 had 151 mg TKN L<sup>-1</sup> was made up of 65 mg TAN L<sup>-1</sup>, and 86 mg L<sup>-1</sup> of organic N (Table 5). However, N losses could occur during P

**Table 3**

Effect of increasing pH with lime addition on TP concentration and corresponding percentage of TP removed as precipitate from the liquid extract in step 2 (lime with no polymer addition) and step 3 (lime plus anionic polymer) of the quick wash process.

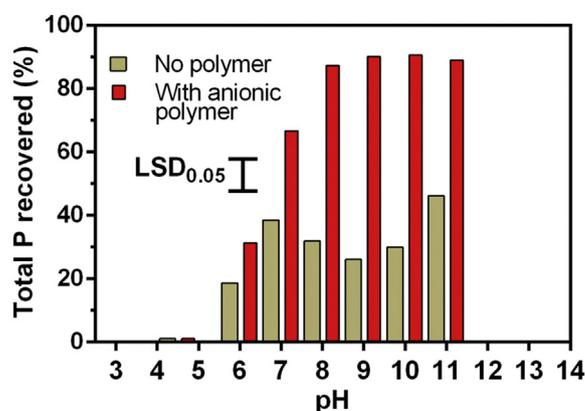
Lime treatment <sup>a</sup>		TP in liquid extract			
pH	Applied time	No polymer (step 2)		With anionic polymer <sup>b</sup>	
	(g L <sup>-1</sup> )	(mg L <sup>-1</sup> )	(% Removed) <sup>c</sup>	(mg L <sup>-1</sup> )	(% removed)
4.5	0.0	256	0	256	0
6.0	0.9	204	19	168	34
7.0	1.4	148	38	68	74
8.0	1.6	166	32	9	96
9.0	1.9	183	26	2	99
10.0	2.2	172	30	0.1	99
11.0	3.1	125	51	5	98
LSD <sub>0.05</sub> <sup>d</sup>		43	17	14	5

<sup>a</sup> Hydrated lime (2% w/v Ca(OH)<sub>2</sub>) added to obtain a specific pH.

<sup>b</sup> Anionic polyacrylamide (34% mole charge) applied at 7 mg L<sup>-1</sup> (a.i.).

<sup>c</sup> TP removed = % P removed from liquid fraction relative to initial P concentration in liquid extract (lime treatment 0).

<sup>d</sup> Least square difference (LSD) value is for comparison of any two means within the same column.



**Fig. 3.** Total P recovered as percentage of initial TP (7.1 g kg<sup>-1</sup>) in fresh manure solids at increasing pH in step 2 (lime addition with no polymer), and step 3 (lime plus anionic polymer – polyacrylamide) of the quick wash. The acid extract at pH 4.5 (control) did not have lime treatment.

**Table 4**

Quick wash process (steps 2 and 3), hydrated lime plus polymer application for recovery of extracted soluble P from pig manure solids.

Lime treatment <sup>a</sup>				
pH	Lime applied	TP recovered in precipitate		
	(g L <sup>-1</sup> )	(g kg <sup>-1</sup> manure)	(%) <sup>b</sup>	(% P <sub>2</sub> O <sub>5</sub> ) <sup>c</sup>
4.5	0.0	0	0	–
6.0	0.9	2.2	31	8.0
7.0	1.4	4.7	67	11.0
8.0	1.6	6.2	87	12.8
9.0	1.9	6.4	90	12.3
10.0	2.2	6.4	90	11.3
11.0	3.1	6.3	89	9.9
LSD <sub>0.05</sub> <sup>d</sup>		0.4	5	1.3

<sup>a</sup> Hydrated lime [2% w/v Ca(OH)<sub>2</sub>] added to obtain a specific pH.

<sup>b</sup> Total P recovered in precipitate = TP in the precipitated solids relative to initial P content in fresh manure (7.1 g kg<sup>-1</sup> wet weight, 70% moisture).

<sup>c</sup> Expressed in dry weight.

<sup>d</sup> Least square difference (LSD) value compares any two means within the same column.

recovery because at ambient temperature and pressure, alkaline pH is a major factor for N loss from the liquid as volatilized ammonia-N (Szögi et al., 2006b).

#### 3.5. Total N and P mass flows

The mass flow balance included the N and P mass input (100% = 9.9 g TN kg<sup>-1</sup> and 7.1 g P kg<sup>-1</sup> in fresh pig manure) and

**Table 5**

Composition of the liquid left after recovering phosphorus from pig manure using the quick wash process (Step 3).

Lime applied	pH	TSS	TKN	TAN	Organic N	TP	RP	
(g L <sup>-1</sup> )		(g L <sup>-1</sup> )	(mg L <sup>-1</sup> )					
0.0	4.46	2.29	269	80	80	256	185	
0.9	6.35	3.06	183	68	68	168	151	
1.4	6.96	3.84	145	67	67	68	66	
1.6	8.00	4.86	151	65	65	9	7	
1.9	9.14	4.97	146	57	57	2	2	
2.2	10.01	5.25	146	48	48	0.1	0	
3.1	10.90	5.11	138	43	43	5	0	
LSD <sub>0.05</sub> <sup>a</sup>		0.13	0.57	18	6	21	14	2

<sup>a</sup> Least square difference (LSD) value compares any two means within the same column.

**Table 6**  
Mass flow balance for N and P as percentage of the initial content of TN and TP in manure at the optimum conditions of the quick wash process.<sup>a</sup>

Nutrient	Inflow	Quick wash outflow <sup>b</sup>			
	Initial manure	Washed residue	Recovered P material	Effluent	Unaccounted
TN	100.0	32.0 ± 1.5 <sup>c</sup>	23.0 ± 1.0	38.1 ± 0.1	6.9 ± 0.8
TP	100.0	9.8 ± 0.8	86.9 ± 1.8	3.3 ± 2.5	0

<sup>a</sup> Optimum quick wash conditions: 10 mmol L<sup>-1</sup> citric acid for P extraction and P recovery at pH 8.0 plus anionic PAM.

<sup>b</sup> Refer to Fig. 1.

<sup>c</sup> Data are the mean of duplicate tests ± one standard deviation.

outputs from the first to the last step of the process (Fig. 1). The mass flow balance for N and P as percentage of the initial content of TN and TP in manure solids is presented in Table 6 for the particular case of optimum conditions of the quick wash process (10 mmol L<sup>-1</sup> citric acid for P extraction, pH 8.0 plus anionic polymer for P recovery). The N mass flow balance of the quick wash process revealed that TN was distributed as follows: 32% remained in the washed manure solids, 23% was recovered in the P precipitate, 38% remained in the effluent, and about 7% was unaccounted and possibly lost due to ammonia volatilization (Table 6).

In the case of the TP mass flow balance, only 10% remained in the washed solids, 87% was recovered in the in the P precipitate, and 3% remained in the effluent. The N remaining in the effluent along with the very low TP concentration suggests that effluents of the quick wash could be either recycled into the quick wash process or effectively land applied for crop production at agronomic N rates with minimal gaseous losses of N. Indeed, recycling of treated swine wastewater effluents could offset the impacts of utilizing large quantities of well and surface waters for growing crops while at the same time not excessively overloading the crops and soils with nutrients (Stone et al., 2010). In a similar way, the treated process effluent flowing back into the influent of the quick wash process could reduce the consumption of higher quality water without burdening local water resources.

### 3.6. Integration of quick wash process into pig manure management systems

The techniques for P recovery from waste streams can be grouped into two types of processes: 1) recovery from liquid phase; and 2) recovery from solids such as sludge ash (Desmidt et al., 2015). The most common techniques for P recovery from the liquid phase of manures include the use of crystallizers and fluid bed reactors with seeding material to promote aggregation of phosphate particles for effective recovery by filtration devices (Karunanithi et al., 2015). The P not recovered from the liquid phase is present in manure solids which can be recovered after thermal treatment followed by a wet chemical process similar to those for recovery from liquid phase (Heilmann et al., 2014). Instead, the quick wash approach combines in a wet chemical process the recovery of P from both liquid and solid phase but it does not require the use of fluid bed reactors and seeding material to promote aggregation of phosphate particles or thermochemical treatment prior extraction and recovery of P from manure solids. Our results on recovering P from solid pig manure using the quick wash process indicate that it can be adapted to manure management systems that collect manure with little or no addition of liquid such as deep pits, deep bedding, scrape, and belt systems (Gentry et al., 2002; Parker, 2011; Koger et al., 2014). The recovery of P into valuable manure byproducts may benefit farmers by reducing the cropland area needed for manure P disposal plus the value of the N contained in the washed manure solids and the recovered P material. In our study, the chemical cost to extract and precipitate P from pig manure solids using the quick wash process was calculated on the

basis of treating one metric ton of pig manure assuming the following conditions:

- Fresh manure containing 9.9 kg N, and 16.3 kg P<sub>2</sub>O<sub>5</sub> per metric ton with 70% moisture.
- The quick wash treatment is done on-farm with an average recovery efficiency for P of 80%; 70% of TN remains on-farm and effluents are used as liquid fertilizer for crop production on the same farm.
- Citric acid is used in step 1 to remove P from pig manure at a rate of 1.92 g L<sup>-1</sup> (Table 1).
- Lime is used at a rate of 1.6 g Ca(OH)<sub>2</sub> L<sup>-1</sup> to attain a pH 8.0 in step 2.
- The chemical costs include the cost of citric acid (US\$ 0.60 kg<sup>-1</sup>), dry lime (US\$ 0.20 kg<sup>-1</sup>), and anionic polymer (US\$ 3.00 kg<sup>-1</sup>)

The amount of P recovered using the quick wash approach would be about 13.0 kg P<sub>2</sub>O<sub>5</sub> with a fertilizer value of US\$22.43 (US\$1.72 kg<sup>-1</sup> of P<sub>2</sub>O<sub>5</sub>). To process one metric ton of pig manure, the quick wash would use 4.8 kg of citric acid at a cost of US\$2.88 for the P extraction (step 1), and 40 kg of lime and 0.35 kg anionic polymer for the P recovery (steps 2 and 3) at a cost of US\$ 8.00 and US\$ 1.05, respectively. With a total chemical cost of US\$ 11.93 ton<sup>-1</sup> of treated pig manure, the net benefit would be of US\$10.50 per ton. As an additional benefit, a total of about 6.9 kg of N (US\$1.42 per kg of N) and 3.3 kg P<sub>2</sub>O<sub>5</sub> at an equivalent value of US\$15.45 per ton of processed manure solids remain on-farm (washed litter plus effluent) and used as crop fertilizer. A complete economic study for on-farm deployment of this technology still requires taking into account annualized capital, energy, and labor costs as well as other benefits such as reduction of land area needed for manure P disposal and additional income from participating in nutrient trading programs (Shortle, 2013).

## 4. Conclusions

Results of this study support the technical feasibility of using the quick wash process to recover P from pig waste. The quick wash process selectively removed and recovered up to 90% of the TP from pig manure solids while leaving significant amounts of N in the washed manure residue. As a result of P manure extraction, the washed manure solid residue had a more balanced N:P ratio for crop production and was environmentally safe for land application on a N basis. With increasing fertilizer costs, this technology has the potential to provide on-farm recovery and concentration of P in valuable byproducts. The recovery of P in concentrated form can make its transfer to P-deficient lands more cost-effective and provide a recycled P source for use as crop fertilizer while minimizing manure P losses into the environment.

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