

## ABSTRACT

KANG, JI-HOON. Phosphorus Leaching in the Coastal Plain Soils of North Carolina. (Under the direction of Deanna Osmond and Dean Hesterberg.)

Some soils in areas of intensive livestock farming have shown significant phosphorus (P) leaching. The objectives of this research were: i) to examine the relationships between soil properties and P sorption capacity, ii) to investigate leaching of P as affected by fertilizer sources, iii) to examine the effects of manure-derived dissolved organic carbon (DOC) on P sorption, and iv) to evaluate deep leaching of P.

The P sorption maximum ( $S_{\max}$ ) of seventy two soil samples from various horizons of Coastal Plain soils of North Carolina (NC) was determined according to the Langmuir equation. Soil samples were analyzed for pH, clay content, organic matter (OM) content, oxalate extractable Al ( $Al_{\text{ox}}$ ), Fe ( $Fe_{\text{ox}}$ ), and P ( $P_{\text{ox}}$ ), Mehlich-3 extractable Al ( $Al_{\text{M3}}$ ), Fe ( $Fe_{\text{M3}}$ ), and P ( $P_{\text{M3}}$ ). The  $S_{\max}$  was positively correlated with extractable Al ( $r = 0.76$  for  $Al_{\text{ox}}$  and  $r = 0.86$  for  $Al_{\text{M3}}$ ) and OM content ( $r = 0.61$ ). The positive linear relationship between OM and  $S_{\max}$  showed a change point where there was a two-fold decrease in the regression slope for  $OM > 42 \pm 4 \text{ g kg}^{-1}$ . Results indicated that Al and Fe in organic-rich soils were likely to be less accessible for P sorption compared to those in mineral soils.

Leaching of P as affected by fertilizer sources was investigated with repacked soil columns (10-cm long). The fertilizer sources were dairy lagoon liquid (DL), poultry compost (PC), poultry litter (PL), swine lagoon sludge (SS), swine lagoon liquid (SL), triplesuperphosphate (TSP), and dissolved  $\text{KH}_2\text{PO}_4$  (KP). When these fertilizer sources were applied on a total P basis (75 and 150 kg ha<sup>-1</sup>) as a pulse, inorganic P sources (TSP and KP) showed about two-fold greater P loss than organic P sources (PC, PL, SL and SS). The loss of source-derived P was well correlated with water extractable P in source materials ( $r^2 = 0.87$ ). Enhanced P transport was observed in the soil columns treated with liquid wastes as compared to the KP.

Concurrent sorption of P and DOC was investigated with batch sorption experiments using the aqueous extracts of PL and SS in Autryville sandy loam. The presence of manure-derived DOC did not inhibit P sorption, while the sorption of DOC decreased in the presence of manure-derived P. Results suggested that the formation of new surface sites through metal bridges between manure-derived OM and mineral oxides outweighed the competitive efficacy of DOC against P on the soil sorption sites.

Deep leaching of P was evaluated with intact soil columns (90-cm long) collected from the Coastal Plain regions of NC. The selected sites were dominated by Autryville loamy sand, Cape Fear loam, and Goldsboro fine sandy loam, and Wasda

muck. A limited pore volume of leached water ( $2.1 \pm 0.1$ ) resulted in low concentration of dissolved reactive P in most column leachates ( $< 0.02 \text{ mg L}^{-1}$ ) except Wasda muck ( $0.034 \text{ mg L}^{-1}$ ). The increased P concentration in Wasda muck was attributable to the higher Mehlich-3 P concentration in deep subsoils ( $22$  to  $69 \text{ mg kg}^{-1}$  at  $75\text{-}90$  cm depth) than the other soils ( $0$  to  $7 \text{ mg kg}^{-1}$  at  $75\text{-}90$  cm depth).

**PHOSPHORUS LEACHING IN THE  
COASTAL PLAIN SOILS OF NORTH CAROLINA**

by

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## **BIOGRAPHY**

Ji-Hoon Kang was born in Seoul, Korea on December 24, 1975. He grew up in Seoul and attended Kyunghee University in Korea. It was here that he became familiar with water quality issues while working as a research student for the wastewater treatment plant unit operation. He went through two years of mandatory military service in the middle of undergraduate education. He received his B.S. in environmental science and engineering in 2001. Upon graduation, Ji-Hoon decided to continue to study in US. He started his master's program at Pennsylvania State University in Fall of 2001 under the direction of Dr. Herschel Elliot in Agricultural and Biological Engineering. During the period of his master's program, he became more interested in water quality issues regarding P losses from soil to water. Upon graduation in 2003, Ji-Hoon started his PhD program at North Carolina State University where he solely focused on soil science under the direction of Drs. Deanna Osmond and Dean Hesterberg.

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## CHAPTER 1

### Phosphorus Sorption Capacity in the Coastal Plain Soils of North Carolina

#### INTRODUCTION

In areas with intensive livestock farming, soils are often enriched with phosphorus (P) as a result of continued applications of fertilizers and animal manures (Pautler and Sims, 2000). The P accumulation in soils and subsequent loss of P from soil to waterways can accelerate eutrophication of surface waters (Sharpley et al., 2003). The potential desorbability of soil P has been well correlated with soil P saturation which estimates the degree to which P sorption sites have been filled (Beauchemin and Simard, 1999; Zhang et al., 2005). In chemical terms, P saturation is defined as the amount of P as a fraction of total P sorption capacity of a soil. The P sorption capacity, a measure of the ability of soil to retain P mainly by adsorption and precipitation, is therefore an important factor controlling the release of P from soil to water.

In non-calcareous soils, P sorption mainly takes place with poorly ordered or non-crystalline forms of Al and Fe (as hydroxides and Al and Fe bound to organic matter) (Beauchemin and Simard, 1999; Schoumans, 2000; Maguire and Sims, 2002). These reactive forms of Al and Fe can be extracted with acid ammonium oxalate solution (pH 3) in the dark. The P sorption capacity (PSC in  $\text{mmol kg}^{-1}$ ) of non-calcareous sandy soils can

be approximated as:

$$\text{PSC} = \alpha (\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}}) \quad [1]$$

where  $\alpha$  is a dimensionless scaling factor, and  $(\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})$  is the sum of oxalate extractable Al and Fe ( $\text{mmol kg}^{-1}$ ). The scaling factor,  $\alpha$ , has been calculated in various studies but a value of 0.5 is normally assumed (Freese et al., 1992; Daly et al., 2001).

Oxalate extractable ( $\text{P}_{\text{ox}}$ ) is often used as an estimate of P already sorbed by the soil and the degree of P saturation ( $\text{DPS}_{\text{ox}}$ ) is estimated by:

$$\text{DPS}_{\text{ox}} = 100 \times \frac{\text{P}_{\text{ox}}}{0.5 (\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})} \quad [2]$$

Based on desorption characteristics of non-calcareous sandy soils, Van der Zee et al. (1988) reported that the P concentration in pore water will become higher than  $0.1 \text{ mg L}^{-1}$  at a  $\text{DPS}_{\text{ox}}$  of 25%. Instead of assuming P sorption capacity as  $0.5 (\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})$ , an independent P saturation index ( $\text{PSI}_{\text{ox}}$ ) can be used as in Eq. (3) and a  $\text{PSI}_{\text{ox}}$  value of 12.5 % is identical to the  $\text{DPS}_{\text{ox}}$  of 25 % (Schoumans, 2000).

$$\text{PSI}_{\text{ox}} = 100 \times \frac{\text{P}_{\text{ox}}}{\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}}} \quad [3]$$

Oxalate extraction is not a routine procedure in most soil testing laboratories. Routine agronomic tests (e.g., Mehlich-3) have been used to calculate an index that ideally correlates with oxalate-based indices (Beauchemin and Simard, 1999; Maguire and Sims, 2002). For example, P saturation index ( $\text{PSI}_{\text{M3}}$ ) based on Mehlich-3 extractable P, Al, and Fe can be estimated as:

$$\text{PSI}_{\text{M3}} = 100 \times \frac{\text{P}_{\text{M3}}}{\text{Al}_{\text{M3}} + \text{Fe}_{\text{M3}}} \quad [4]$$

where  $\text{P}_{\text{M3}}$ ,  $\text{Al}_{\text{M3}}$ , and  $\text{Fe}_{\text{M3}}$  are Mehlich-3 extractable P, Al, and Fe in  $\text{mmol kg}^{-1}$ , respectively.

Acid organic soils of the Coastal Plain of southern US have been shown to contain tremendous amounts of Al and Fe and therefore higher P sorption capacity than other organic soils without significant Al contents (Richardson, 1985). Increased formation of metal bridges between Al and organic matter (OM) may be attributable to increased P sorption through ternary complexes of OM-Al-P on mineral surfaces (Guppy et al., 2005; Giesler et al., 2005; Dell'Olio, 2006). In contrast, P sorption can be also affected by competitive sorption between dissolved P and dissolved organic matter (DOM) for soil sorption sites (e.g., poorly-crystalline Al and Fe). Low molecular organic acids present in organic-rich soils have been found to compete with P for the sorption sites, resulting in a net decrease in P sorption (Hue, 1991; Bhatti et al., 1998). The effects of organic matter on P sorption are controversial, having these two contradictory reports on the P sorption characteristics in organic-rich soils or soils amended with organic wastes.

Traditionally, P sorption capacity of a soil has been determined in the laboratory by equilibrating the soil with a range of P concentrations for a set period of time. Linearized form of Langmuir equation is often used to calculate the P sorption maximum

( $S_{\max}$ ) of the soil (Graetz and Nair, 2000). Since determining P sorption isotherm is a sample-intensive process, many efforts has been made to use  $Al_{ox}$  and  $Fe_{ox}$  or  $Al_{M3}$  and  $Fe_{M3}$  to approximate the P sorption capacity of a soil (Pautler and Sims, 2000; Maguire and Sims, 2002; Kleinman and Sharpley, 2002; Nair et al., 2004; Zhang et al., 2005; Penn et al., 2006). Our study was initiated to characterize the PSC of selected mineral and organic-rich mineral soils from the Coastal Plain regions of NC. We compared the  $S_{\max}$  from the Langmuir isotherms with the PSC estimated from oxalate extraction and Mehlich-3 extraction, respectively. Based on the P sorption characteristics from organic-rich soils (Johnson, 2004; Dell'Olio, 2006), we hypothesized that mineral-organic soils have unique P sorption characteristics compared to other mineral soils. The objectives of this study were (i) to compare Mehlich-3 and oxalate extraction for Al, Fe and P, (ii) to determine  $S_{\max}$  and its correlation with other soil properties, and (iii) to examine the influences of OM on  $S_{\max}$ .

## **MATERIALS AND METHODS**

### **Soil collection**

Four soil series were selected for this study, representing mineral soils (Autryville and Goldsboro) and mineral-organic soils (Cape Fear and Wasda) in the Coastal Plain of NC: Autryville (loamy, siliceous, subactive, thermic Arenic Paleudults), Goldsboro (fine-loamy, siliceous, subactive, thermic Aquic Paleudults), Cape Fear (fine, mixed, semiactive, thermic Typic Umbraquults) and Wasda (fine-loamy, mixed, semiactive, acid, thermic Histic Humaquepts). For each mapping unit, we selected three sites with different P application history: triplesuperphosphate (TSP), poultry litter (PL) and swine lagoon liquid (SL). From each field (12 total fields), soil samples were collected from 0-15, 15-30, 30-45, 45-60, 60-75 and 75-90 cm depth to include surface and subsoil samples. A total of 72 soil samples were air-dried and ground to pass a 2-mm sieve.

### **Soil analysis**

Particle size distribution was determined by the hydrometer method (Gee and Bauder, 1986). Soil pH was measured in a 1:1 water to soil ratio with a glass electrode, and soil OM was determined by loss-on-ignition (Nelson and Sommers, 1996). Soil samples were analyzed for (i) Mehlich-3 extractable P, Al, and Fe (1:10 soil to Mehlich-3

extracting solution, 0.2 M CH<sub>3</sub>COOH + 0.25 M NH<sub>4</sub>NO<sub>3</sub> + 0.015 M NH<sub>4</sub>F + 0.013 M HNO<sub>3</sub> + 0.001 M EDTA, filtration through Whatman #42 filter paper) (Mehlich, 1984) and (ii) ammonium oxalate extractable P, Al, and Fe (1:40 soil to ammonium oxalate extraction solution at pH 3.0 in the dark, centrifuging, filtration through 0.45- $\mu$ m membrane) (Schoumans, 2000). The Mehlich-3 and oxalate extracts were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

### **Phosphorus sorption isotherm**

Batch P sorption isotherms were determined according to the method of Graetz and Nair (2000). One gram of soil was equilibrated with 25 mL of varying concentration of P in 0.01 M KCl solution in 50-mL centrifuge tubes. The input concentrations of equilibrating P solutions were 0, 0.5, 2.5, 5, 10, 25, 50 and 230 mg P L<sup>-1</sup>. Since P sorption is pH dependent (Barrow, 1984), soil pH was employed as one of soil properties affecting P sorption, and accordingly the pH adjustment on the soil suspension was not made. The tubes were shaken for 24-h on a reciprocating shaker at 120 cycles per minute (cpm) and supernatants were filtered through 0.45- $\mu$ m membrane. The filtrates were analyzed colorimetrically by the molybdate blue method (Murphy and Riley, 1962).

The total amount of P sorbed on the soil was calculated as:

$$S = S' + S_o \quad [5]$$

where  $S$  = total amount of P sorbed in the soil ( $\text{mmol kg}^{-1}$ ),  $S_0$  = initially sorbed P, and  $S'$  = amount of added P sorbed by the soil ( $\text{mmol kg}^{-1}$ ). The  $S'$  in a soil was determined by:

$$S' = \frac{[(C_0 \times V) - (C \times V)]}{M} \quad [6]$$

where  $C_0$  = concentration of P in input solution ( $\text{mmol L}^{-1}$ ),  $V$  = volume of liquid (L),  $C$  = concentration of P in final solution after 24-h equilibration ( $\text{mmol L}^{-1}$ ), and  $M$  = mass of soil (kg). The  $S_0$  was empirically estimated from the linear relationship between  $S'$  and  $C$  at low P concentrations using the least square fit method (Graetz and Nair, 2000; Pant and Reddy, 2001). The P sorption maximum ( $S_{\max}$ ) and bonding energy constant ( $K_L$ ) were calculated using a linearized form of the Langmuir equation by (Graetz and Nair, 2000):

$$\frac{C}{S} = \frac{C}{S_{\max}} + \frac{1}{K_L S_{\max}} \quad [7]$$

where  $S_{\max}$  = P sorption maximum ( $\text{mmol kg}^{-1}$ ) and  $K_L$  = a constant related to the bonding energy ( $\text{L mmol}^{-1}$ ). By regressing  $C/S$  against  $C$ , the slope is equal to  $1/S_{\max}$  and the intercept is equal to  $1/(K_L S_{\max})$ .

### **Statistical analysis**

All correlation, regression and analysis of variance were performed by standard procedures of SAS version 8.2 (SAS Institute, 2001). The split-line regression (NLIN) procedure within SAS was used to determine the change point between OM and  $S_{\max}$ .

## RESULTS AND DISCUSSION

### Soil characteristics

In NC, Autryville and Goldsboro soils are classified as mineral soils while Cape Fear and Wasda soils are classified as mineral-organic soils based on their OM content (Tucker and Rhodes, 1987). The study soils were moderately acidic with the pH ranging from 4.4 to 6.0 (Table 1). The mean pH of the mineral-organic soils ( $4.9 \pm 0.1$ ; mean  $\pm$  standard error) was lower than mineral soils ( $5.2 \pm 0.1$ ). When averaged by all depths, mineral-organic soils exhibited greater mean OM ( $96 \pm 16 \text{ g kg}^{-1}$ ) than mineral soils ( $21 \pm 2 \text{ g kg}^{-1}$ ). Clay content in the soils ranged from 18 to 335  $\text{g kg}^{-1}$  with the greater mean clay content in mineral soils ( $86 \pm 11 \text{ g kg}^{-1}$ ) than mineral-organic soils ( $70 \pm 12 \text{ g kg}^{-1}$ ).

### Relationships between Mehlich-3 and oxalate extractable Al, Fe and P

Phosphorus extracted by Mehlich-3 ( $P_{M3}$ ) and ammonium oxalate method ( $P_{ox}$ ) varied by soil and sampling depth, ranging from 0 to 13.1  $\text{mmol } P_{M3} \text{ kg}^{-1}$  and 0.1 to 22  $\text{mmol } P_{ox} \text{ kg}^{-1}$ , respectively (Table 1). Ranges of  $Al_{M3}$  were from 17.3 to 94.6  $\text{mmol kg}^{-1}$  and  $Al_{ox}$  were from 4.0 to 256.5  $\text{mmol kg}^{-1}$ . The  $Fe_{M3}$  ranged from 0.4 to 8.9  $\text{mmol kg}^{-1}$  while  $Fe_{ox}$  were from 0.7 to 55.6  $\text{mmol kg}^{-1}$ . On average, Mehlich-3 extracted 50% of  $P_{ox}$ , 35% of  $Fe_{ox}$  and 178 % of  $Al_{ox}$ .

Figure 1 shows the relationship between  $Al_{ox}$  and  $Al_{M3}$  segmented by soil types,



where the differences of extractable Al between the two extractants were pronounced among soil types. In mineral soils, Mehlich-3 extracted about two-fold greater amounts of Al (mean  $Al_{M3}/Al_{ox} = 2.03 \pm 0.21$ ) than oxalate. Penn et al. (2006) noted that Mehlich-3 was able to extract some portion of crystalline Al due to the presence of  $NH_4F$  (0.015 M). The electronegative fluoride (F) ion is known to replace  $-OH/H_2O$  groups bound to surficial Al atoms, loosens crystalline Al-OH bonds, and facilitates the dissolution of crystalline Al-oxides (Harrington et al., 2003).

In contrast, oxalate extracted greater amounts of Al (mean  $Al_{M3}/Al_{ox} = 0.79 \pm 0.23$ ) than Mehlich-3 in mineral-organic soils. Acid organic-rich soils in the Coastal region of southeastern US have been reported to contain organically bound Al, which is attributable to the release by mineral dissolution and rapid readsorption of  $Al^{3+}$  to organic matter (McBride, 1994). Moreover, the presence of organic acids in organic-rich soils is known to hinder the formation of crystalline Al hydroxides, keeping more Al in a non-crystalline form (Borggaard et al., 1990; Masion et al., 1994). Accordingly, some of  $Al_{ox}$  in mineral-organic soils may have been derived from non-crystalline Al complexed by OM.

Overall, less Fe (in  $mmol\ kg^{-1}$ ) was extracted from the study soils as compared with Al, the effect being more pronounced in the Mehlich-3 extractant (Figure 2). The mean molar ratio of  $Al_{M3}/Fe_{M3}$  ( $32 \pm 3.5$ ) were about six-fold greater than that of oxalate

( $Al_{ox}/Fe_{ox} = 5.0 \pm 0.9$ ) with a greater difference in mineral soils ( $Al_{M3}/Fe_{M3} = 45 \pm 5.8$ ).

Thermodynamics explanation is possible for this disproportionately less extraction of Fe compared to Al. For example, at pH 2.5 (solution pH in the Mehlich-3 extractant), the solubility of non-crystalline  $Al(OH)_3$  is about  $10^5$  times greater than that of poorly-crystalline  $Fe(OH)_3$  (Lindsay, 1979). The extractability of Fe between Mehlich-3 and oxalate extractants segmented by soil types is provided in Figure 3. Oxalate was able to extract about three-fold greater amounts of Fe from the soils than Mehlich-3, showing higher Fe concentrations especially in mineral-organic soils. Compared to oxalate, Mehlich-3 was a weak extractant for Fe, which is in agreement with other studies (Maguire and Sims 2001; Johnson, 2004; Zhang et al., 2005).

Phosphorus extracted by oxalate and Mehlich-3 is shown in Figure 4, where the differences of extractable P between the two extractants were pronounced among soil types. Overall Mehlich-3 extracted 86% of  $P_{ox}$  in mineral soils and 32% of  $P_{ox}$  in mineral-organic soils, indicating that Mehlich-3 is a weak extractant especially in removing P retained via OM-metal cation bridging (e.g.,  $PO_4-Al-OM$  and  $PO_4-Fe-OM$ ). In theory, oxalate anion replaces P sorbed at metal-hydroxide surfaces through ligand exchange reactions, and it complexes metals in solution and thus prevents precipitation of metal phosphates (Fox et al., 1990). Readsorption of dissolved P in the oxalate extract is, therefore, less likely than in the Mehlich-3, because of the formation of complexed Fe

and Al, and because Ca precipitated by the oxalate anion causes less precipitation and readsorption of phosphates as Ca-P (Fox et al., 1990; Borggaard et al., 1992). The acidity of oxalate makes its mode of P extraction similar to that of HCl (Gao and Yost, 1999).

Based on Eq.[2] and Eq.[3], we estimated the PSI using both oxalate ( $PSI_{ox}$ ) and Mehlich-3 ( $PSI_{M3}$ ) as extractants. The  $PSI_{ox}$  values ranged from 0 to 58% and  $PSI_{M3}$  values ranged from 0 to 36%. The  $PSI_{M3}$  were linearly related to the  $PSI_{ox}$  with  $r^2$  of 0.96 ( $p < 0.001$ ) when all data from mineral and mineral-organic soils were combined. Our result is consistent with other researchers who have reported the highly significant relationships between  $PSI_{ox}$  and  $PSI_{M3}$  (Kleinman and Sharpley, 2002; Maguire and Sims, 2002; Zhang et al., 2005). In our study, the value of  $PSI_{M3}$  corresponding to 12.5 % of  $PSI_{ox}$  was 7.1%, which is close to 6.8% reported by Maguire and Sims (2002). Our results suggest that the  $PSI_{M3}$  (7.1 %) will be useful in identifying soils that have a risk of P release from soil to water.

### **Correlation between soil properties and phosphorus sorption maximum**

The P sorption data were satisfactorily described by the linearized Langmuir equation with the coefficients of determination ranging from 0.89 to 0.99. Figure 6 shows an example of P sorption isotherm fitted with Langmuir equation in the topsoils segregated by soil series. The  $S_{max}$  ranged from 1 to 64  $mmol\ kg^{-1}$  with a greater mean in

mineral-organic soils ( $29 \pm 2 \text{ mmol kg}^{-1}$ ) than mineral soils ( $15 \pm 2 \text{ mmol kg}^{-1}$ ) (Table 1). The correlation matrix between  $S_{\text{max}}$  ( $\text{mmol kg}^{-1}$ ), soil pH, clay ( $\text{g kg}^{-1}$ ), OM ( $\text{g kg}^{-1}$ ), Al, Fe and sum of Al and Fe ( $\text{mmol kg}^{-1}$ ) is presented in Table 2. The correlation matrix in Table 2 was segregated by extractable Al and Fe by oxalate and Mehlich-3 extraction, namely the oxalate model and the Mehlich-3 model, respectively. Significant positive correlations ( $p < 0.01$ ) were observed between the  $S_{\text{max}}$  and all soil properties (clay, OM, Al and Fe) except soil pH. Soil pH had a native correlation with the  $S_{\text{max}}$  ( $r = -0.54$ ) which is consistent with findings by others (Oh et al., 1997; Hingston et al., 1972) in that P sorption was found to decrease with increasing pH in soil minerals. As a single variable,  $\text{Al}_{\text{ox}}$  in the oxalate model and  $\text{Al}_{\text{M3}}$  in Mehlich-3 model had the highest Pearson correlation coefficients with  $S_{\text{max}}$  ( $r = 0.76$  and  $0.86$ , respectively). The correlation between  $\text{Fe}_{\text{M3}}$  and  $S_{\text{max}}$  ( $r = 0.21$ ) was not significant as compared to the significant positive correlation between  $\text{Fe}_{\text{ox}}$  and  $S_{\text{max}}$  ( $r = 0.6$ ,  $p < 0.01$ ) due to low Fe extraction efficacy of Mehlich-3 (Figure 3, and Maguire and Sims, 2002; Johnson 2004). Significant correlation between OM and Al was better observed with  $\text{Al}_{\text{ox}}$  ( $r = 0.87$ ) than  $\text{Al}_{\text{M3}}$  ( $r = 0.59$ ). This result is indicative of Al associated with OM. Soil clay ( $r = 0.46$ ) and OM ( $r = 0.61$ ) had a positive correlation with  $S_{\text{max}}$ , which may be due to the indirect effects of Al and Fe on  $S_{\text{max}}$  via clay and OM (Zhang et al., 2005; Ige et al., 2007).

### **Multiple regressions describing the relationship between soil properties and P sorption maximum**

It is well known that multicollinearity occurs when predictor variables are so highly correlated, resulting in the coefficient estimates that have larger variances with consequent lack of statistical significance (Freund and Littell, 2000). For diagnostic purposes, the condition index (CI) was used to assess the influence of multicollinearity between predictor variables in the multiple linear regressions. This could be calculated using an option in the SAS statistical package, with CI values  $> 30$  denoting serious multicollinearity (Belsley et al., 1980). For the regression equations used in this study, the calculated CI values were small (2.5 to 8.4), suggesting that the regression equations presented in Table 3 were not affected largely by the multicollinearity.

Stepwise multiple regressions were performed to identify the soil properties that contribute most to P sorption maximum at a probability level of 0.0001 (Table 3). We performed two series of multiple regressions where one series contained Al and Fe as a separate variable while the other series contained sum of Al and Fe as a single variable. In both series, the regression results were segmented by oxalate and Mehlich-3 model. A consistent feature of the regression equations in Table 3 was that Al was the single most important contributor for the  $S_{\max}$  ( $r^2 = 0.57$  and  $0.74$  for oxalate and Mehlich-3 model, respectively).

In the two-term regression equations, clay was identified as second most

important contributor for  $S_{\max}$  by increasing  $r^2$  from 0.57 to 0.88 in the oxalate model and from 0.74 to 0.82 in the Mehlich-3 model. The contribution of clay in predicting  $S_{\max}$  may be attributable to the crystalline oxides of Al and Fe in the clay fraction that were not extracted by both extractants. It is notable that the regression equations from both extractants did not identify Fe as second most important contributor for  $S_{\max}$ . The reason for this result is, again, due to the relative low extractable Fe compared to Al in soils (molar  $Al_{ox}/Fe_{ox} = 5.4 \pm 0.1$  and molar  $Al_{M3}/Fe_{M3} = 32.1 \pm 3.5$ ). The oxalate model did not have a significant three-term regression equation while the Mehlich-3 model did with  $Al_{M3}$ , clay and OM ( $r^2 = 0.86$ ). Possible reason for this result is that since Mehlich-3 is a weak extractant for organically bound Al, inclusion of OM in the regression better explained the variability of  $S_{\max}$  by improving  $r^2$  from 0.82 to 0.86.

Even though a comparison of the regression equations in Table 3 implied that extractable Fe was not as significant as Al in predicting  $S_{\max}$ , it would be unrealistic to accept the regression implication that soil Fe did not influence the P sorption (Adams et al., 1997). In some soils in which Al-oxides dominates P sorption, the removal of the Al-oxides yielded P sorption being dominated by the Fe-oxides content of the soil (Bromfield, 1965). The results from stepwise regressions having sum of Al and Fe as a single predictor are also presented in Table 3. The coefficient of determination for the regression equations in Table 3 were not greatly improved compared to the equations

with Al and Fe as separate variables. Therefore, we conclude that extractable Al plays a key role over extractable Fe in estimating  $S_{\max}$  in the Coastal Plain soils of NC.

### **Influence of organic matter on P sorption capacity**

Figure 7 shows the relationship between  $[Al_{ox} + Fe_{ox}]$  and  $S_{\max}$  segregated by mineral and mineral-organic soils. Linear regressions for each soil type resulted in significantly different linear relationships ( $p < 0.001$ ) between  $S_{\max}$  and  $[Al_{ox} + Fe_{ox}]$ . The  $S_{\max}$  increased by 0.68 per unit increase of  $[Al_{ox} + Fe_{ox}]$  in mineral soils while it did only by 0.28 in mineral-organic soils. This suggests a lower  $S_{\max}$  in mineral-organic soils than mineral soils if both soils have the same amount of  $[Al_{ox} + Fe_{ox}]$ .

Figure 8 compares the scaling factor ( $\alpha$ ) from each series of soils calculated as the ratio of PSC (here  $S_{\max}$  was used) to  $[Al_{ox} + Fe_{ox}]$  as in Eq. [1]. The Autryville soil had an  $\alpha$  value of  $0.5 \pm 0.08$ , which is very similar to the 0.48 value determined by Van der Zee et al. (1990) for acid, sandy, low organic matter topsoils in the Netherlands. The Goldsboro soil had an  $\alpha$  value of  $0.64 \pm 0.08$ , which was not significantly different with that of Autryville ( $p < 0.01$ ). Mineral-organic soils, however, had significantly lower  $\alpha$  value ( $0.36 \pm 0.03$  for Cape Fear and  $0.31 \pm 0.03$  for Wasda) than mineral soils, suggesting that organically bound Al and Fe in mineral-organic soils are likely to be less accessible for P sorption compared to those in mineral soils.

Figure 9 shows the relationship between OM and  $S_{\max}$  segregated by mineral and mineral-organic soils. A change point in OM ( $42 \pm 4 \text{ g kg}^{-1}$ ) was identified where two different linear relationships between OM and  $S_{\max}$  were observed. In  $\text{OM} < 42 \text{ g kg}^{-1}$ , the slope of linear regression of OM against the  $S_{\max}$  was 0.73 while the slope in  $\text{OM} > 42 \text{ g kg}^{-1}$  was 0.33, showing about a two-fold difference in the regression slopes. The positive correlation between OM and  $S_{\max}$  is consistent with previous studies in that accumulation of Al and Fe in organic-rich soils can increase the P sorption capacity (Bloom, 1981; Gerke and Hermann, 1992; Giesler et al., 2005; Dell'Olio, 2006). For example, Gerke and Herman (1992) noted that organically bound Al (III) and Fe (III) had a greater P sorption capacity than non-crystalline oxides of Al and Fe and crystalline oxides of Al and Fe not associated with OM. The decreased  $S_{\max}$  beyond the change point ( $\text{OM} = 42 \pm 4 \text{ g kg}^{-1}$ ) may be explained by the finding of Hesterberg and Hutchison (2006) who showed that when organically bound Al (III) and Fe (III) exceeded the available surface functional groups (e.g., carboxylic and phenolic acid) in soil OM, some metal ions clustered together, making the metal ions inaccessible for P sorption.



## CONCLUSIONS

Since P sorption maximum by batch isotherms and oxalate extraction are not routinely performed in most soil testing laboratories, we examined the use of Mehlich-3 as an alternative for these procedures. Our data for 72 samples from the selected soils from the Coastal Plain regions of NC showed that Mehlich-3 was a stronger extractant for Al than oxalate in mineral soils and oxalate was a stronger extractant than Mehlich-3 in mineral-organic soils. Both mineral and mineral-organic soils had lower extractable Fe concentration as compared with Al, the effect being more pronounced in the Mehlich-3 extractable Fe. Comparison of extractable P by oxalate and Mehlich-3 implies that oxalate is a stronger extractant than Mehlich-3, pronounced in mineral-organic soils. The  $PSI_{M3}$  was very well correlated with  $PSI_{ox}$ , having a threshold of  $PSI_{M3}$  at 0.71%, regardless of soil types, suggesting that the  $PSI_{M3}$  may serve a useful but less-sensitive index in identifying soils with increased risk for P loss.

Extractable Al and OM in the soils were highly correlated with the  $S_{max}$  by a simple correlation. Multiple linear regressions of soil properties against the  $S_{max}$  in both the oxalate and the Mehlich-3 models revealed that extractable Al was the most important components in predicting  $S_{max}$ . The coefficient of determination of multiple linear regression ( $r^2$ ) was improved with inclusion of clay in the oxalate model ( $r^2 = 0.86$ ) while with inclusion of clay and OM in the Mehlich-3 model ( $r^2 = 0.89$ ). These results indicated

that the estimation of  $S_{\max}$  using  $(Al_{\text{ox}} + Fe_{\text{ox}})$  may underestimate the influence of crystalline oxides of Al and Fe while the use of  $(Al_{\text{M3}} + Fe_{\text{M3}})$  may underestimate the influences of crystalline oxides of Al and Fe but also organically bound Al and Fe on  $S_{\max}$ .

A split-line linear relationships was observed between OM and  $S_{\max}$ , where there was a two-fold decrease in regression slope for  $OM > 42 \pm 4 \text{ g kg}^{-1}$ . Our result is in agreement with previous studies in that the P sorption capacity of organic-rich soils with appreciable amounts of Al increased, presumably due to organically bound Al. Results indicated that Al and Fe in organic-rich soils were likely to be less accessible for P sorption compared to those in mineral soils.

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**Table 1. Soil properties and P sorption characteristics for all 72 soil samples.**

Soil	P source history	Depth cm	Soil pH	Clay	Organic matter		P <sub>M3</sub> †	Al <sub>M3</sub> †	Fe <sub>M3</sub> †	P <sub>ox</sub> ‡	Al <sub>ox</sub> ‡	Fe <sub>ox</sub> ‡	S <sub>max</sub> §	K <sub>L</sub> ¶	PSI <sub>M3</sub> #	PSI <sub>ox</sub> ††
					g kg <sup>-1</sup>	g kg <sup>-1</sup>										
Autryville	TSP	0-15	6.4	10.8	6.9	6.6	25.4	2.7	6.2	11.9	4.2	2.9	2.9	2.3	38.7	
		15-30	6.0	21.5	3.9	3.1	24.9	1.7	3.2	8.9	2.9	2.0	15.7	11.5	27.3	
		30-45	5.3	31.0	3.6	0.9	27.9	1.2	0.9	5.8	2.0	2.8	5.5	3.0	12.1	
		45-60	5.1	22.5	3.2	0.5	28.0	0.9	0.6	5.3	1.6	3.1	15.7	1.7	9.1	
		60-75	4.9	43.5	5.8	0.2	40.9	0.7	0.3	7.9	1.6	5.5	21.5	0.4	3.0	
		75-90	4.8	43.6	5.4	0.2	40.4	0.6	0.2	7.4	1.5	6.1	29.7	0.4	2.8	
	Poultry	0-15	5.3	17.1	9.6	6.6	24.6	2.1	7.1	11.3	3.7	1.6	7.9	24.8	47.6	
		15-30	4.9	25.5	6.0	5.6	27.4	1.9	5.6	11.3	3.2	2.3	68.2	19.2	38.3	
		30-45	4.7	40.9	5.7	3.2	30.2	1.0	3.5	9.3	2.2	4.5	3.9	10.1	30.2	
		45-60	4.5	143.3	24.5	1.3	54.5	0.6	2.6	34.1	5.4	35.2	18.9	2.3	6.5	
		60-75	4.5	145.8	23.1	0.0	52.5	0.5	0.4	32.6	5.7	47.4	30.1	0.1	1.0	
		75-90	4.8	150.8	22.8	0.1	47.5	0.4	0.4	28.2	5.5	38.9	42.8	0.1	1.3	
Swine	0-15	6.4	12.7	9.9	6.5	19.5	2.9	5.6	9.3	3.6	1.8	2.3	29.1	43.0		
	15-30	7.0	8.9	4.8	4.8	18.1	2.5	5.2	9.0	3.4	3.6	0.8	23.5	41.6		
	30-45	6.9	27.0	2.6	1.3	18.1	1.2	1.3	4.0	1.6	0.9	12.9	6.6	22.9		
	45-60	6.6	50.8	7.6	0.5	32.8	1.0	0.8	9.8	4.4	5.9	6.3	1.4	5.7		
	60-75	5.4	74.6	11.5	0.2	44.4	0.9	0.5	14.1	6.4	16.9	7.9	0.4	2.2		
	75-90	5.5	32.7	4.7	0.2	39.0	0.8	0.4	7.0	4.5	9.5	8.6	0.6	3.8		
Cape Fear	TSP	0-15	5.8	15.4	31.3	3.8	61.5	5.4	7.5	75.6	22.2	21.7	7.9	5.7	7.7	
		15-30	5.4	22.8	27.7	1.8	60.0	5.2	3.6	59.3	22.9	25.1	12.1	2.8	4.4	
		30-45	4.6	198.3	26.8	0.1	63.6	3.9	0.4	60.8	56.6	40.3	31.0	0.1	0.3	
		45-60	4.7	241.7	32.5	0.1	71.1	3.1	0.4	66.7	39.4	45.5	27.5	0.2	0.4	
		60-75	4.7	228.7	31.9	0.2	71.0	2.6	0.4	66.7	23.6	43.5	17.7	0.2	0.4	
		75-90	4.6	194.3	29.2	0.1	67.2	2.7	0.3	59.3	32.2	43.5	6.6	0.2	0.4	
	Poultry	0-15	6.1	15.6	28.5	3.9	44.7	4.1	6.8	41.5	12.9	10.3	5.6	8.0	12.6	
		15-30	5.8	15.4	25.5	2.5	52.9	3.7	4.6	50.4	10.7	14.8	5.1	4.4	7.6	
		30-45	4.8	16.0	18.7	0.2	54.7	2.5	0.5	48.9	9.3	21.3	58.6	0.4	0.9	
		45-60	4.7	22.5	21.9	0.2	57.3	2.4	0.4	48.9	14.3	28.5	19.5	0.3	0.6	
		60-75	4.7	165.1	23.5	0.2	52.3	2.0	0.4	38.5	13.6	27.2	10.2	0.3	0.7	
		75-90	4.7	159.6	20.7	0.1	44.2	1.6	0.3	31.1	17.2	24.7	10.7	0.3	0.6	
Swine	0-15	5.9	18.3	47.5	8.9	49.7	5.1	19.4	57.8	19.3	18.7	3.8	16.2	25.1		
	15-30	5.8	20.6	39.6	3.4	60.4	4.5	6.6	65.2	15.8	20.0	8.3	5.2	8.1		
	30-45	5.1	13.5	26.2	1.6	67.9	4.2	3.6	81.5	32.2	33.3	27.3	2.3	3.2		
	45-60	4.9	185.9	27.3	0.7	68.6	4.0	1.5	69.7	25.8	42.0	23.8	1.0	1.6		
	60-75	4.9	188.4	26.3	0.7	62.9	3.8	1.3	59.3	25.1	39.4	15.9	1.1	1.5		
	75-90	4.8	194.0	26.3	0.2	64.1	3.6	0.8	63.7	44.4	40.8	20.4	0.4	0.8		
Goldsboro	TSP	0-15	5.0	44.5	10.8	9.5	24.4	3.3	11.8	14.8	5.6	67.1	2.2	34.3	57.6	
		15-30	5.4	157.2	10.7	13.1	32.5	3.8	14.2	20.8	5.6	2.3	15.3	36.0	53.9	
		30-45	4.9	187.1	18.8	4.6	43.1	1.4	6.2	26.7	6.5	14.9	4.4	10.3	18.7	
		45-60	4.5	204.4	18.5	0.3	36.4	0.7	0.8	20.8	5.5	20.1	14.6	0.9	2.9	
		60-75	4.5	255.3	18.3	0.0	37.8	0.5	0.1	16.3	2.7	22.5	15.3	0.1	0.6	
		75-90	4.4	238.8	18.5	0.1	36.4	0.6	0.2	14.7	2.1	17.8	11.7	0.3	1.2	
	Poultry	0-15	6.1	17.3	13.3	11.3	26.7	4.7	14.2	17.8	7.9	7.6	0.8	35.8	55.3	
		15-30	5.7	32.3	18.7	5.2	38.1	2.8	7.0	22.2	6.2	11.0	3.4	12.7	24.6	
		30-45	4.7	114.5	22.3	0.7	50.7	0.7	1.1	31.1	4.5	26.0	15.4	1.3	3.2	
		45-60	4.5	114.5	23.1	0.1	50.0	0.5	0.3	32.6	4.7	31.6	9.3	0.3	0.9	
		60-75	4.4	139.2	28.2	0.0	52.6	0.4	0.1	37.1	4.7	37.0	9.3	0.1	0.3	
		75-90	4.4	130.2	26.7	0.1	54.5	0.6	0.2	38.5	4.0	35.0	19.1	0.1	0.6	
Swine	0-15	5.2	29.6	16.4	1.6	40.1	3.5	3.9	31.1	12.9	10.3	8.8	3.8	8.8		
	15-30	4.7	104.6	13.3	0.2	40.6	1.6	0.4	23.7	9.3	17.8	8.6	0.4	1.3		
	30-45	4.5	99.8	12.1	0.1	36.2	0.9	0.2	17.8	6.0	17.6	11.8	0.2	0.8		
	45-60	4.5	101.1	13.3	0.0	62.1	1.3	0.2	22.2	7.9	20.0	12.5	0.1	0.6		
	60-75	4.5	101.4	12.2	0.0	37.7	0.8	0.2	20.8	7.0	20.3	12.3	0.1	0.6		
	75-90	4.5	126.8	15.9	0.0	35.9	0.5	0.1	20.8	5.3	24.3	19.6	0.0	0.3		
Wasda	TSP	0-15	4.4	9.5	143.6	4.7	66.3	4.0	14.2	145.3	23.6	46.1	2.4	6.7	8.4	
		15-30	4.2	17.3	98.0	6.3	94.6	3.1	22.0	256.5	15.0	64.1	9.8	6.5	8.1	
		30-45	4.2	12.4	42.4	1.8	77.9	1.2	5.2	97.8	2.7	36.0	19.9	2.2	5.1	
		45-60	4.3	7.5	21.6	0.7	48.9	0.6	1.2	47.4	1.0	19.0	13.1	1.4	2.5	
		60-75	4.4	65.7	14.1	0.1	30.0	1.7	0.3	20.8	0.7	10.6	15.7	0.2	1.2	
		75-90	4.4	68.6	20.9	0.0	65.1	5.9	0.1	17.8	2.2	12.6	6.5	0.0	0.6	
	Poultry	0-15	5.0	12.3	101.9	4.2	63.4	6.8	16.8	126.0	35.1	37.3	7.2	6.0	10.4	
		15-30	4.8	14.3	97.4	3.3	64.2	7.8	15.5	118.6	32.9	38.2	9.4	4.6	10.2	
		30-45	5.1	11.2	96.5	3.4	63.1	7.7	12.3	140.8	36.5	35.5	14.1	4.7	6.9	
		45-60	5.2	18.0	82.0	2.5	65.0	8.0	10.8	124.5	33.7	38.8	13.6	3.4	6.9	
		60-75	5.1	15.7	72.8	2.2	65.1	8.2	9.4	111.2	33.7	36.0	18.5	3.1	6.5	
		75-90	4.9	10.9	30.7	2.2	49.5	8.9	5.2	48.9	26.5	24.5	8.5	3.8	6.8	
Swine	0-15	4.8	10.3	109.8	3.8	66.7	4.9	12.8	131.9	25.8	39.1	7.5	5.4	8.1		
	15-30	4.8	10.0	49.7	1.2	71.7	2.6	3.4	102.3	10.0	31.4	7.8	1.6	3.0		
	30-45	4.8	12.2	17.4	0.4	40.0	1.5	0.6	41.5	3.2	13.4	9.7	0.9	1.3		
	45-60	4.8	130.1	19.0	0.1	25.0	5.4	0.2	14.8	21.5	14.7	5.3	0.2	0.6		
	60-75	5.0	122.2	16.7	0.1	19.3	4.6	0.3	11.4	26.5	10.0	8.6	0.5	0.7		
	75-90	5.2	62.6	15.4	0.7	17.3	3.5	1.0	11.7	8.6	5.3	5.7	3.4	4.7		
		Mean	5.0	78.2	28.3	2.2	47.2	2.8	4.1	45.4	13.2	22.9	13.8	4.3	7.0	
		Median	4.8	42.2	20.8	0.7	48.2	2.5	1.2	31.1	6.8	20.2	10.4	1.4	3.1	
		Minimum	4.2	7.5	2.6	0.0	17.3	0.4	0.1	4.0	0.7	0.9	0.8	0.1	1.9	
		Maximum	7.0	255.3	143.6	13.1	94.6	8.9	22.0	256.5	56.6	67.1	68.2	12.6	7.0	

† Mehlich-3 extractable P, Al, and Fe, respectively.

‡ Ammonium-oxalate extractable P, Al, and Fe, respectively.

§ P sorption maximum calculated from Langmuir adsorption isotherms.

¶ A constant related to bonding energy.

# P saturation index calculated from Mehlich-3 data as the molar ratio of  $100 \times P_{M3}$  to  $[Al_{M3} + Fe_{M3}]$ .

†† P saturation index calculated from acid ammonium oxalate data as the molar ratio of  $100 \times P_{ox}$  to  $[Al_{ox} + Fe_{ox}]$ .

**Table 2. Correlation matrix (r values) of P sorption maximum and soil properties. Correlation is significant at  $p < 0.01$  for  $r > 0.30$ .**

Oxalate model							
Response	$S_{\max}$	pH	Clay	OM	$Al_{ox}$	$Fe_{ox}$	$Al_{ox} + Fe_{ox}$
$S_{\max}$	1						
pH	-0.54	1					
Clay	0.46	-0.44	1				
OM	0.61	-0.22	-0.19	1			
$Al_{ox}$	0.76	-0.25	-0.12	0.87	1		
$Fe_{ox}$	0.60	-0.10	0.21	0.48	0.58	1	
$Al_{ox} + Fe_{ox}$	0.78	-0.24	-0.05	0.85	0.98	0.72	1

Mehlich-3 model							
Response	$S_{\max}$	pH	Clay	OM	$Al_{M3}$	$Fe_{M3}$	$Al_{M3} + Fe_{M3}$
$S_{\max}$	1						
pH	-0.54	1					
Clay	0.46	-0.44	1				
OM	0.61	-0.22	-0.19	1			
$Al_{M3}$	0.86	-0.45	0.22	0.59	1		
$Fe_{M3}$	0.22	0.18	-0.30	0.51	0.33	1	
$Al_{M3} + Fe_{M3}$	0.85	-0.41	0.17	0.62	0.99	0.43	1



**Table 3. Multiple linear regression equations describing the relationship between soil properties and P sorption maximum ( $S_{\max}$ ) in study soils (n = 72).**

Extractant	Regression equations	$r^2$ †	Regression equations	$r^2$ †
	<u>Al and Fe as separate variables</u>		<u>Sum of Al and Fe as a single predictor</u>	
Oxalate	$S_{\max} = 10.41 + 0.25 (Al_{ox})$	0.57	$S_{\max} = 9.04 + 0.22 (Al_{ox} + Fe_{ox})$	0.61
model	$S_{\max} = 0.77 + 0.27 (Al_{ox}) + 0.07 (Clay)$	0.88	$S_{\max} = 0.88 + 0.23 (Al_{ox} + Fe_{ox}) + 0.06 (Clay)$	0.86
Mehlich-3	$S_{\max} = -13.01 + 0.74 (Al_{M3})$	0.74	$S_{\max} = -12.91 + 0.70 (Al_{M3} + Fe_{M3})$	0.72
model	$S_{\max} = -14.96 + 0.69 (Al_{M3}) + 0.03 (Clay)$	0.82	$S_{\max} = -15.69 + 0.65 (Al_{M3} + Fe_{M3}) + 0.04 (Clay)$	0.83
	$S_{\max} = -11.13 + 0.48 (Al_{M3}) + 0.05 (Clay) + 0.07 (OM)$	0.86	$S_{\max} = -11.52 + 0.46 (Al_{M3} + Fe_{M3}) + 0.05 (Clay) + 0.06 (OM)$	0.89

† Regression coefficients significant at a probability of 0.0001.

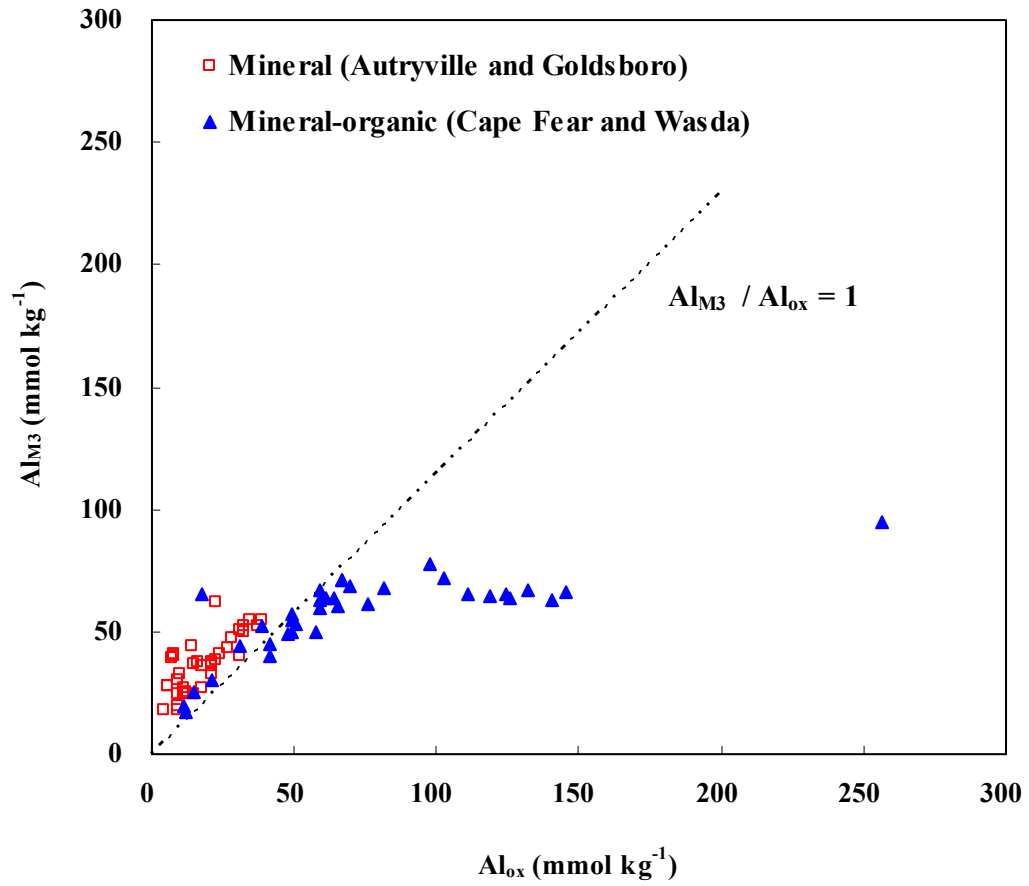
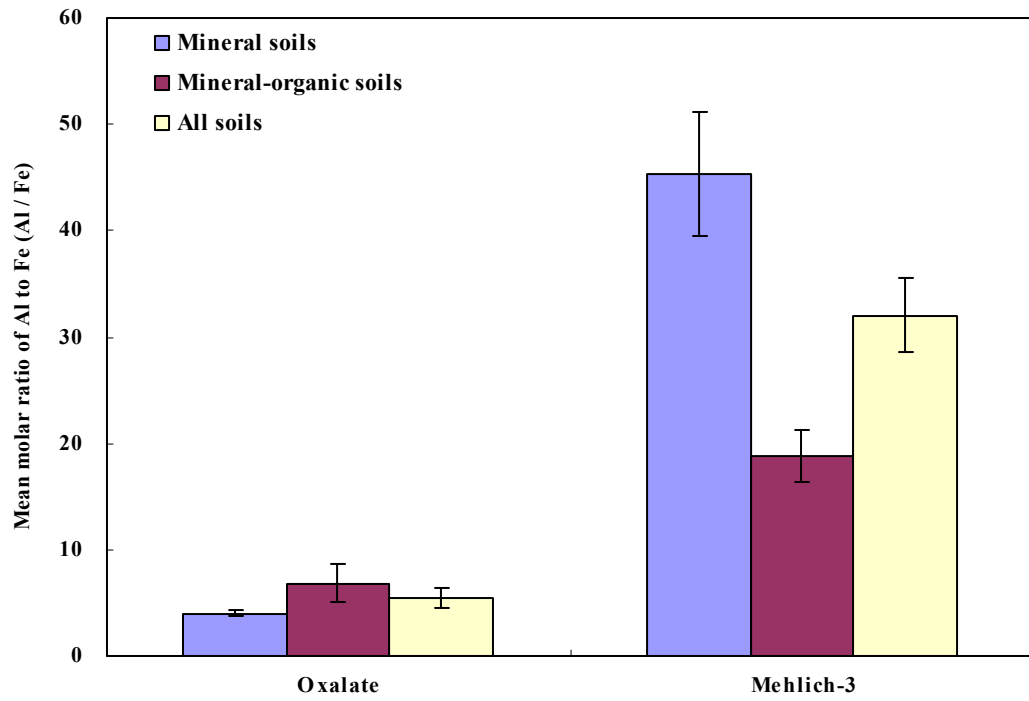


Figure 1. Comparison of oxalate extractable Al ( $Al_{ox}$ ) to Mehlich-3 extractable Al ( $Al_{M3}$ ).



**Figure 2. Comparison of mean molar ratio of Al to Fe between oxalate and Mehlich-3 extraction.**

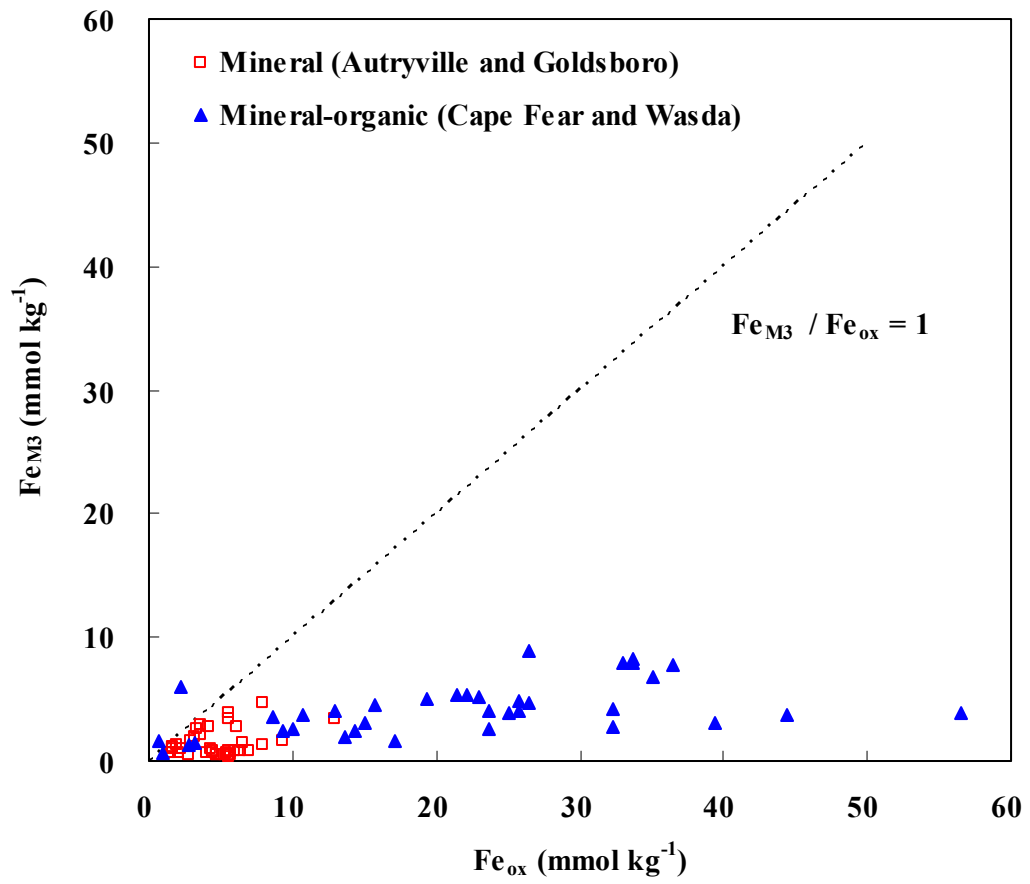


Figure 3. Comparison of oxalate extractable Fe ( $\text{Fe}_{\text{ox}}$ ) to Mehlich-3 extractable Fe ( $\text{Fe}_{\text{M3}}$ ).

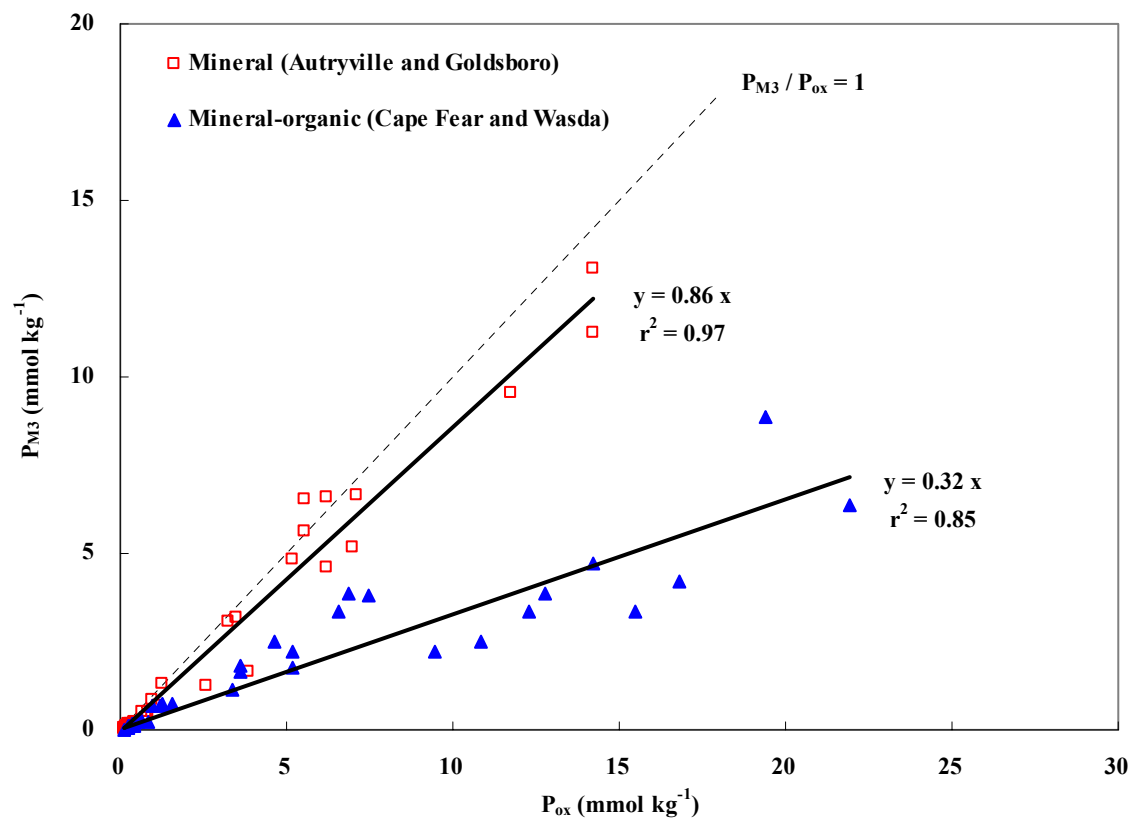
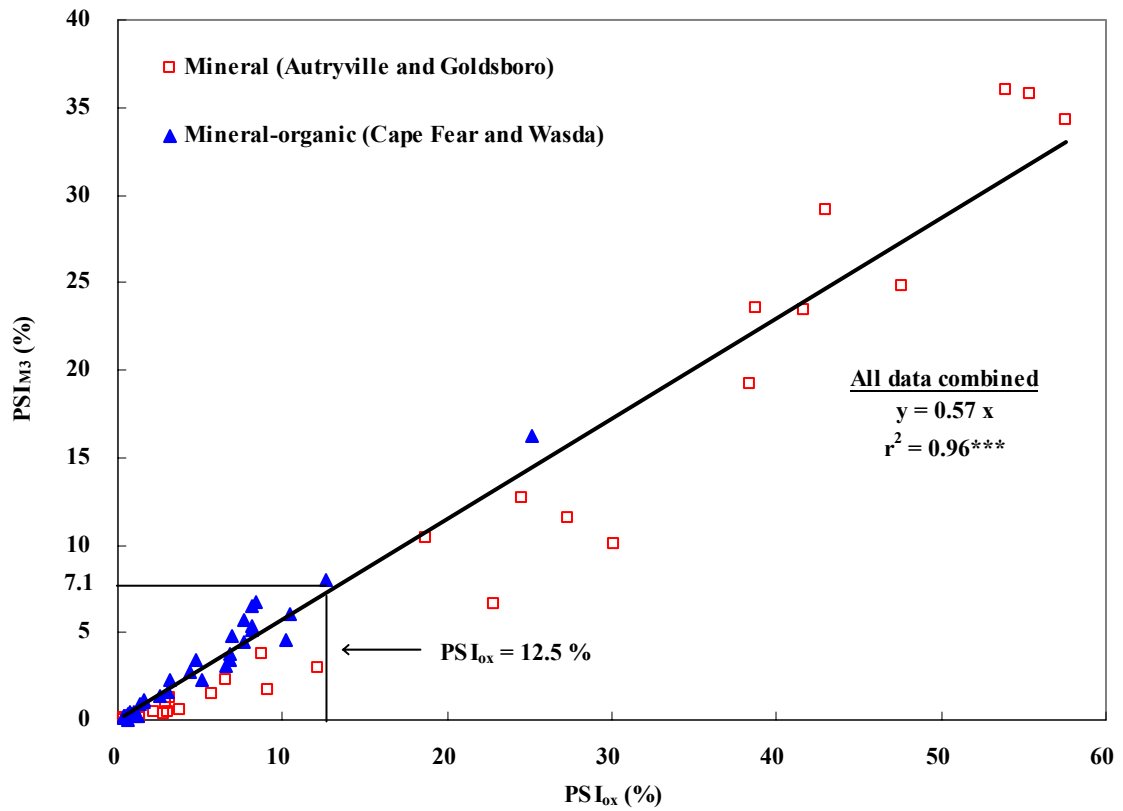
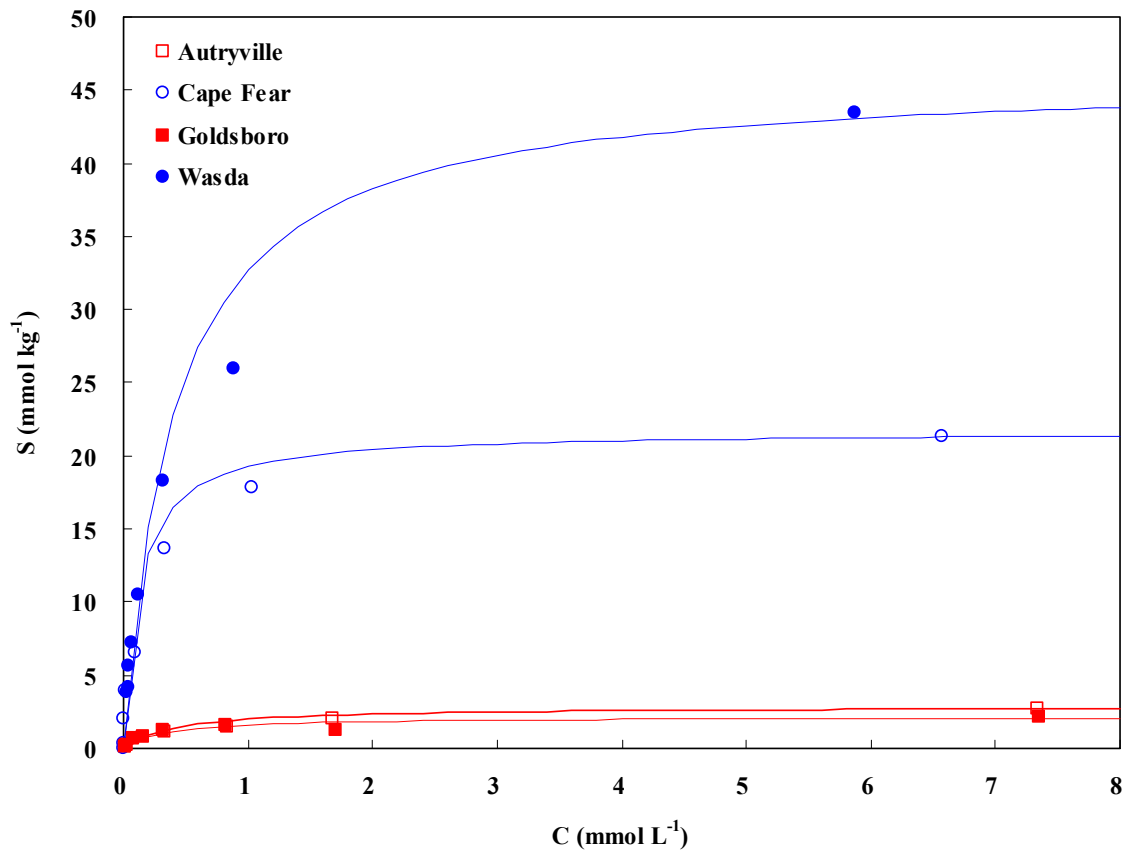


Figure 4. Comparison of oxalate extractable P ( $P_{ox}$ ) to Mehlich-3 extractable P ( $P_{M3}$ ).



**Figure 5. Relationship between phosphorus saturation indexes by oxalate ( $PSI_{ox}$ ) and by Mehlich-3 ( $PSI_{M3}$ ).**



**Figure 6. Phosphorus sorption data fitted with the Langmuir equation. C is P concentration in solution, and S is P sorbed to the soil. Data from topsoil (0-15 cm) in each soil were used.**

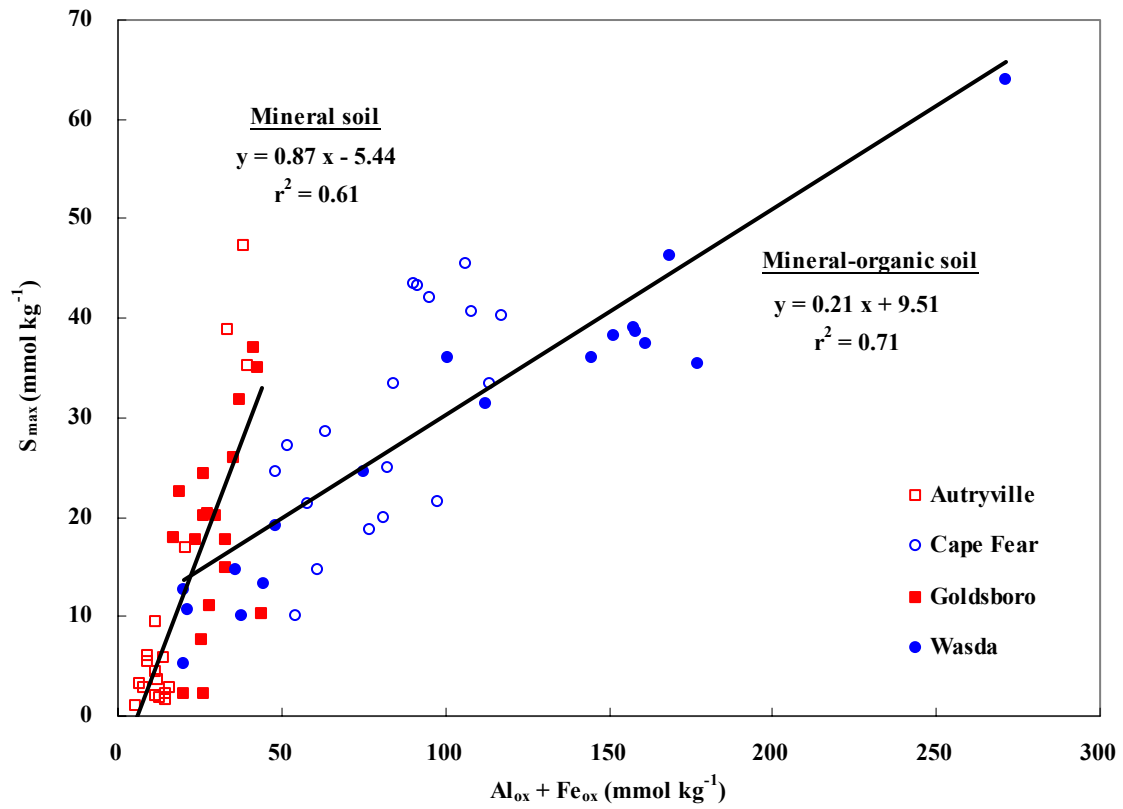
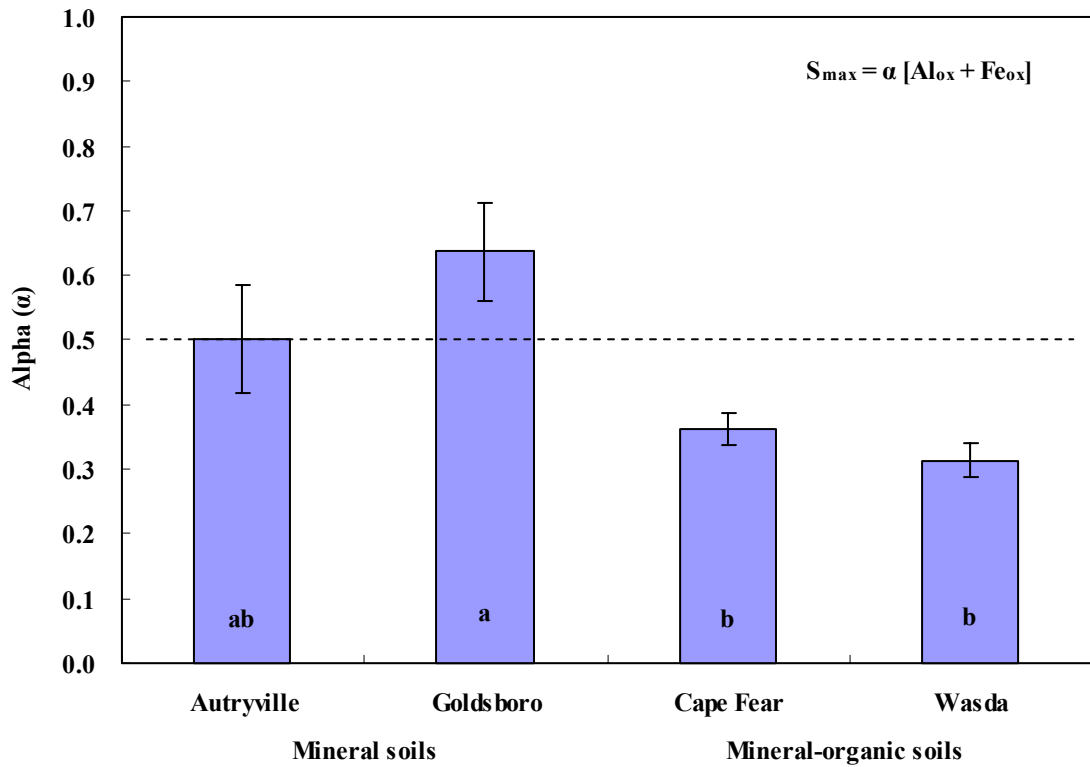


Figure 7. Relationship between  $[Al_{ox} + Fe_{ox}]$  and  $S_{max}$  segregated by mineral and mineral-organic soils.





**Figure 8. The scaling factor ( $\alpha$ ) estimated from soils used. Means followed by the same letter are not significantly different according to the Fisher's Least Significant Difference at a probability level of 0.01.**

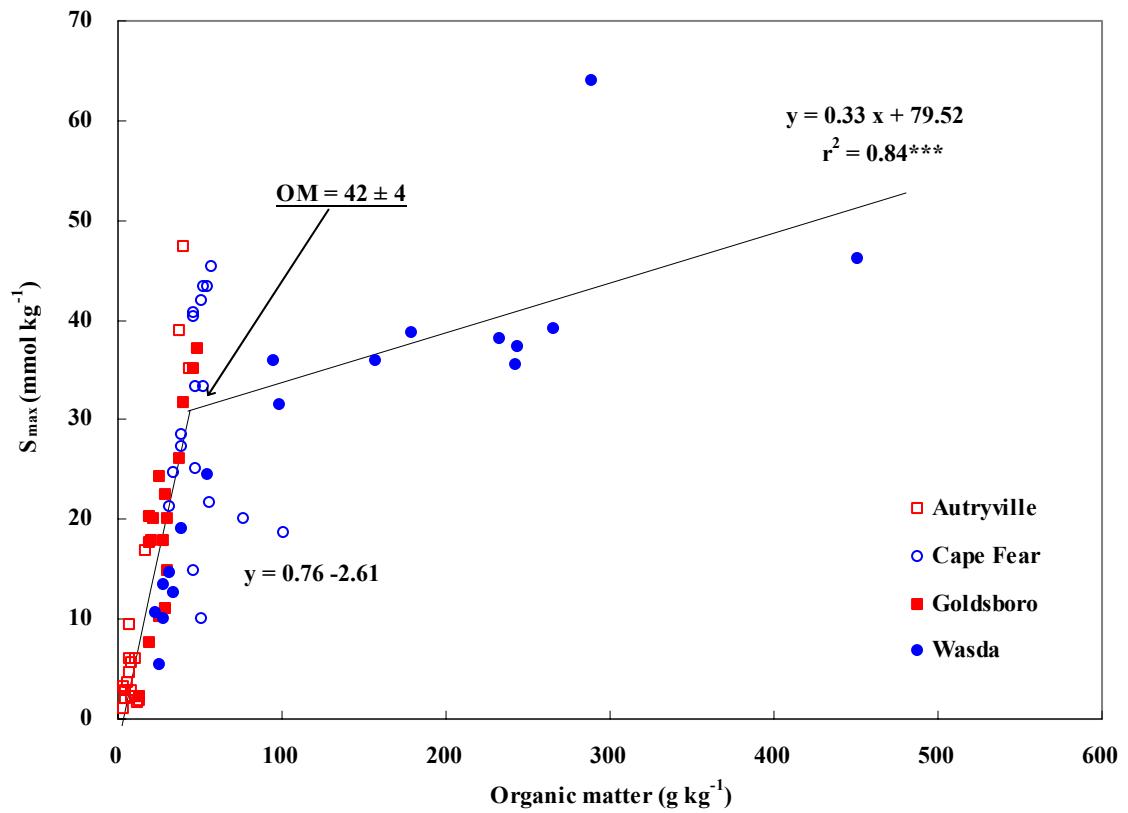


Figure 9. Relationship between organic matter content and  $S_{max}$  segregated by mineral and mineral-organic soils.

## CHAPTER 2

### Phosphorus Leaching as Affected by Fertilizer Sources

#### INTRODUCTION

Phosphorus (P) loss following heavy application of animal wastes to agricultural lands has been a major contributor to eutrophication of surface waters (Sharpley et al., 1999). Total P concentrations in animal wastes vary widely as a function of manure type, nutrient diet, and waste handling and storage (NC PLAT committee, 2005). The P in animal wastes is present in both inorganic and organic forms. Organic P content in animal wastes varies with animal species, age and diet, but typically comprises 5 to 25 % of total P (Sharpley and Moyer, 2000; Mullins et al, 2005). Sharpley and Moyer (2000) found that the inorganic P fraction of total P is 63% for dairy manure, 93% for dairy compost, 85% for poultry manure, 87% for poultry compost, 87% for poultry litter and 91% for swine slurry, suggesting that most P in animal wastes consists of inorganic P.

Water-extractable P (WEP) has been used as an index for the solubility of P source materials and has been linked to dissolved reactive P (DRP) loss in surface runoff and in subsurface drainage (McDowell and Shapley, 2001; Kleinman et al., 2002). Kleinman et al. (2002) applied dairy, chicken, and swine manures at a rate of 100 kg total P ha<sup>-1</sup> to three acidic soils using packed soil boxes with simulated rainfall. They found

that DRP in runoff was strongly related to WEP in manures ( $\text{DRP}^{0.5} = \text{y-intercept} + 0.34 \times \text{WEP}$ ,  $r^2 = 0.86$ ; y-intercept differs between manure types,  $p < 0.01$ ). Similarly, Sharpley and Moyer (2000) measured leachable P from animal wastes when subjected to simulated rainfall. They related the WEP with cumulative P loss by leaching in all five rainfall events and yielded:  $\text{DRP loss (g kg}^{-1} \text{ manure)} = 0.47 \text{ WEP (g kg}^{-1} \text{ manure)} + 1.00$ ,  $r = 0.98$ . They concluded that the potential of P to be leached from animal wastes was most closely related to the WEP of the respective materials. They also found that cumulative P loss (leachable P) followed the order of dairy manure > poultry manure > poultry compost > dairy compost = swine slurry.

Chardon et al. (1997) conducted a laboratory column study to examine the short-term effect of a single, heavy cattle slurry application ( $350 \text{ kg P ha}^{-1}$ ) on leaching of dissolved organic P (DOP) in a sandy soil. They found that 0.5 % of the total amount of P applied with slurry was leached during the study period and more than 96% of the P leached from the slurry-treated soil was DOP. Concentration of DOP ranged from 1.0 to  $2.0 \text{ mg L}^{-1}$  for the slurry-treated column compared to that of control (0.004 to  $0.03 \text{ mg L}^{-1}$ ). This study concluded that while solution phase P in animal wastes is a small percentage of total P, significant amount of the solution phase P may be in organic forms, and therefore more mobile through soil than orthophosphate.

Anderson and Magdoff (2005) performed a laboratory column P leaching study

using specific P substrates, which were 4-methylumbelliferyl phosphate (MUP), deoxyribonucleic acid (DNA), and  $\text{KH}_2\text{PO}_4$ . They added about 2 L of 0.005 M  $\text{CaCl}_2$  over a period of 5-h, and measured four different fractions of P (orthophosphate monoester, orthophosphate diester, inorganic P, and total P). They found that the mass of orthophosphate diesters ( $756 \mu\text{g P } 2\text{L}^{-1}$ ) leached from the DNA columns were greater than that from the MUP columns ( $4.6 \mu\text{g P } 2\text{L}^{-1}$ ) and inorganic P from the  $\text{KH}_2\text{PO}_4$  columns ( $34 \mu\text{g P } 2\text{L}^{-1}$ ). They suggested that repeated application of organic forms of P could result in significant leaching of P to groundwater.

Sandy soils, characterized by a rapid rate of water percolation and low P sorption capacity, are vulnerable to P loss by leaching (Sims et al., 1998; Nelson et al., 2005). Conceptually leaching of P can be conceived to proceed via two steps: a loading step and a subsequent translocation step (Jensen et al., 1998, 2000). In the loading step, P is “loaded” through its release from the source (e.g., land-applied P source materials) into infiltrating water. In the translocation step, P moves vertically with infiltrated water at different rates depending on organic P mineralization, travel distance, P sorption capacity of the soil, and the presence of preferential flow.

This study was initiated to investigate the loading step affected by a variety of P source materials and the subsequent translocation step in a sandy surface soil. Even though numerous studies examined P sorption isotherm with surface soils by

equilibrating soil with known amounts of P, studies that incorporate P sorption parameters into a solute transport model is scarce. We estimated the P sorption parameters from a batch isotherm experiment and predicted vertical P transport parameters using the CXTFIT program (Toride et al, 1999). The observed P leaching data were then compared to the predicted P transport. The objectives of this study were i) to examine leachability of surface-applied P source materials through soil columns, ii) to relate leachate P with water extractable P in P source materials, and iii) to characterize vertical source-derived P transport through soil columns as compared to the one predicted from a batch P isotherm and the solute transport model.

## **MATERIALS AND METHODS**

### **Soil column preparation**

Soil samples were collected from the surface soil (0-30 cm) of Autryville sandy loam (loamy, siliceous, subactive, thermic Arenic Paleudults) collected from Sampson County, NC. Collected soil samples were air-dried and mixed well using a concrete mixer. The soil was 92.5% sand, 5.4% silt and 2.1% clay with a pH of 4.9 (Table 1). Mehlich-3 extractable P ( $P_{M3}$ ) was  $155.5 \text{ mg kg}^{-1}$ , exceeding a critical agronomic level of  $53 \text{ mg kg}^{-1}$  in NC (Johnson et al., 2005).

Forty five columns (6.35-cm internal diameter and 10-cm length) were carefully packed with 480 g of oven-dried soil (110°C for 18-h, oven-dried to remove initial soil moisture and packed to a bulk density of 1.5 g cm<sup>-3</sup>). Prior to packing, inner surface of the PVC liner was coated with the same soil using a commercial glue (The Gorilla Glue Company, Cincinnati, OH) to minimize side wall flow by creating a rough inner-surface. The bottom of a column was sealed to a funnel (Nalgene Company, Rochester, NY) to allow drainage. Soil columns were wet to surface saturation for a 1-d and then allowed drain for a 1-d before leaching experiment was initiated.

### **Bromide tracer test**

A 40 mL pulse of KBr (50 mg Br L<sup>-1</sup>) was applied to the top of columns followed by DI water irrigation under unsaturated flow condition. The purpose of Br addition was to monitor the presence of preferential flow and the adsorption of Br to the soil. After Br tracer test, soil columns were weighted to determine a water-filled porosity, which represents one liquid capacity (LC) in an unsaturated column (estimated LC = 100 cm<sup>-3</sup>). A total of 320 mL of water was irrigated and leachate Br data was presented in a relative concentration ( $C/C_0$ ) as a function of the number of pore volume (PV) leached water:

$$PV = CV / LC \quad [1]$$

where CV = cumulative volume of column leachate. The CXTFIT program (Toride et al.,

1999) was used to fit the observed Br data to estimate dispersion coefficient (D) and retardation factor (R). The Br concentration in column leachates was measured by the phenol red method using the Lachat QuickChem 8000 (Milwaukee, WI).

### **Phosphorus source mixtures**

Seven P source materials used in this study included solid, semi-solid, and liquid types of inorganic and organic P sources: poultry compost (PC), poultry litter (PL), swine lagoon sludge (SS), and triplesuperphosphate (TSP), dairy lagoon liquid (DL), swine lagoon liquid (SL) and dissolved  $\text{KH}_2\text{PO}_4$  (KP). Organic P sources were chosen to represent common alternatives to inorganic P fertilizers, varying in their physical and chemical characteristics. Animal wastes were collected from the swine, poultry, and dairy education units at Lake Wheeler Road Field Laboratory, Raleigh, NC. On the day of collection, animal waste samples were submitted to the North Carolina Department of Agriculture and Consumer Service testing lab for pH, dry matter, and total elemental concentration (C, N, and P). Selected properties of the P source materials are provided in Table 2. Collected animal wastes were stored at 4°C for further use.

All P source materials were weighed to meet two rates of P load (75 and 150 kg total P  $\text{ha}^{-1}$ ). Solid and semi-solid P source materials were prepared by shaking the respective amounts of P source materials equivalent to the proposed P loads in a 200 mL



of DI water. We used 1-h shaking in a reciprocating shaker at 120 cycles per minute (cpm) similar to the common procedure of water extractable P in manures (Self-Davis and Moore, 2000). Liquid wastes were prepared without dilution corresponding to the proposed P loads. For the analysis of total dissolved P (TDP) and DRP in the prepared P mixtures, the supernatants were centrifuged at  $10,000 \times g$  for 10 min, and filtered through a 0.45- $\mu\text{m}$  membrane. The filtrates were analyzed for the DRP colorimetrically and the TDP by the persulfate digestion method using the Lachat QuickChem 8000 (Milwaukee, WI).

### **Leaching process**

Seven P source materials prepared as a solid-liquid mixture (called hereafter “P mixture”) were surface-applied at the rates of 75 and 150 kg total P ha<sup>-1</sup> following two way factorial arrangements on a completely randomized design (Figure 2). Factor A was the application rates (P load) and factor B was the types of P source materials. Three check columns were included to represent the control treatment, representing no P amendment. Pulse duration, defined in Eq.[2], from solid and semi-solid was 2.0 PV while those from liquid P sources varied depending on their respective amounts to meet the P loads.

$$\text{Pulse duration (PV)} = [\text{Volume of P mixture (mL)}] / [\text{LC (mL)}] \quad [2]$$

All columns received the same amount of water (a total of 2400 mL of liquid that consists of P source mixture and DI water). The 50 mL of water was irrigated on a daily basis and column leachates were collected right before a new irrigation starts. Leachate samples were filtered through a 0.45- $\mu\text{m}$  membrane and analyzed for the DRP and the TDP using the Lachat QuickChem 8000 (Milwaukee, WI). The DOC in the leachate samples was determined by the Shimadzu carbon analyzer (Shimadzu Corp., Tokyo).

### **Phosphorus sorption isotherm**

A batch P sorption isotherm was performed to determine the P sorption parameters of the study soil according to the method of Graetz and Nair (2000). One gram of soil was equilibrated with 25 mL of varying concentration of P in 0.01 M KCl solution in 50-mL centrifuge tubes. The input concentrations of equilibrating P solutions were 0, 0.01, 0.05, 0.1, 0.5, 1, 10, 50, 100, 200, 400 and 1000 mg P L<sup>-1</sup>. The tubes were shaken for 24-h on a reciprocating shaker at 120 cycles per minute (cpm) and supernatants were filtered through a 0.45- $\mu\text{m}$  membrane. The filtrates were analyzed for the DRP colorimetrically using the Lachat QuickChem 8000 (Milwaukee, WI). The total amount of P sorbed on the soil was calculated as:

$$S = S_0 + S' \quad [3]$$

where S = total amount of P sorbed in the soil (mg kg<sup>-1</sup>), S<sub>0</sub> = initial sorbed P and S' =

amount of added P sorbed by the soil ( $\text{mg kg}^{-1}$ ). The  $S'$  in a soil was determined as:

$$S' = \frac{[(C_0 \times V) - (C \times V)]}{M} \quad [4]$$

where  $C_0$  = concentration of P in input solution ( $\text{mg L}^{-1}$ ),  $V$  = volume of liquid (L),  $C$  = concentration of P in final solution after 24-h equilibration ( $\text{mg L}^{-1}$ ), and  $M$  = mass of dry soil (kg). The  $S_0$  was empirically estimated from the linear relationship between  $S'$  and  $C$  at low P concentrations using the least square fit method (Graetz and Nair, 2000; Pant and Reddy, 2001). The P sorption maximum ( $S_{\text{max}}$ ) and bonding energy constant ( $K_L$ ) were determined with the linearized form of Langmuir equation (Graetz and Nair, 2000).

$$\frac{C}{S} = \frac{C}{S_{\text{max}}} + \frac{1}{K_L S_{\text{max}}} \quad [5]$$

where  $S_{\text{max}}$  = P sorption maximum ( $\text{mg kg}^{-1}$ ) and  $K_L$  = a constant related to the bonding energy ( $\text{L mg}^{-1}$ ). By regressing  $C/S$  against  $C$ , the slope is equal to  $1/S_{\text{max}}$  and the intercept is equal to  $1/(K_L S_{\text{max}})$ .

### **Phosphorus transport estimation from the Langmuir sorption model**

The Langmuir sorption parameters were used to estimate retardation factor ( $R_L$ ) for P transport through the soil in saturated flow condition as follows:

$$R_L = 1 + \frac{\rho_b k_d}{\theta_v} \quad [6]$$

where  $k_d$  = sorption partition coefficient ( $\text{L kg}^{-1}$ ),  $\rho_b$  = soil bulk density ( $\text{g cm}^{-3}$ ),  $\theta_v$  =

volumetric water content of the soil ( $\text{cm}^3 \text{ cm}^{-3}$ ). We determined the adsorption partition coefficient,  $k_d$ , by finding the tangent to the Langmuir isotherm at the respective DRP concentration from P source mixtures. Differentiating Eq. [5] with respect to C gives (Akhtar et al., 2003; Mamo et al., 2005):

$$k_d = \frac{dS}{dC} = \frac{1}{1 + K_L C} \left[ K_L S_{\max} - \frac{K_L^2 S_{\max} C}{1 + K_L C} \right] \quad [7]$$

The retardation factor in Eq. [6] and transport parameters estimated from Br data (D and R) were used to predict the transport of P following the one-dimensional convective-dispersive equation (CDE). The CXTFIT 2.1 (Toride et al., 1999) was run to produce the P breakthrough curve with the estimated  $R_L$  in Eq. [6].

### **Statistical analysis**

Analysis of variance using the PROC GLM model was used to evaluate the effects of P source materials and their application rate on cumulative P loss using an *F*-statistic (SAS Institute, 2001).

## RESULTS AND DISCUSSION

### **Bromide tracer test**

The observed Br data from 45 column leachates fitted well with the CXTFIT ( $r^2 = 0.99$ ), confirming that packing of all columns was similar. The Br BTC was symmetrical with only minor tailing indicating that Br moved through soil columns with minimal adsorption or preferential transport (Figure 2). The CXTFIT-fitted transport parameters are provided in Table 3. As seen from retardation factor ( $R = 1.19 \pm 0.01$ ), Br was nearly an inert tracer. The column Peclet number ( $P_e$ ), which relates the effectiveness of mass transport by advection to the effectiveness of mass transport either by dispersion or diffusion, was  $17.0 \pm 1.6$  indicating that advection dominates over diffusion in the soil columns used (Fetter, 1999).

### **Properties of P source mixtures**

The concentrations of TDP, DRP, and DOC varied among the P mixture types and the P loads used (Table 4). The pulse duration of solid and semi-solid P source (PC, PL, SS, and TSP) mixtures was 2 PV at both P loads, while liquid P sources had greater pulse duration following the desired P loads (6.8 to 6.92 PV at high P load and 3.4 to 3.46 PV at medium P load). Within the P mixtures that had a pulse duration of 2 PV, TSP mixture at high P load had the highest DRP ( $200 \text{ mg L}^{-1}$ ), followed by PC ( $65 \text{ mg L}^{-1}$ ), PL

(41 mg L<sup>-1</sup>), and SS (26 mg L<sup>-1</sup>). Among liquid P source materials, KP (65 mg L<sup>-1</sup>) had greater DRP than DL (24 mg L<sup>-1</sup>) and SL (17 mg L<sup>-1</sup>). The mass of dissolved components were generally 2-fold greater in high P load (150 kg TP ha<sup>-1</sup>) than those in medium P load (75 kg TP ha<sup>-1</sup>). Mass of DOC in organic P mixtures except SS was much higher (90-163 mg DOC at high P load) than inorganic P sources (0.8-1.2 mg DOC at high P load). The dissolved P fraction relative to total P from the inorganic P sources (KP and TSP) ranged from 89 to 100 % while that from the organic P mixtures varied from 13 to 38 %, showing the differences in the WEP in the P source materials by the 1-h water extraction procedure. The TDP in the P mixtures was present mostly by DRP (>90% except swine sludge = 83%), indicating that relatively small portions of dissolved organic P (as difference between TDP and DRP) was present in the prepared P mixtures.

### **Leaching of dissolved phosphorus from surface-applied P source mixtures**

The mass of P leached over 2 months (cumulatively, approximately 23 PV of column leachate) from columns amended with seven P source materials at 75 and 150 kg TP ha<sup>-1</sup> is provided in Table 5. The DRP relative to TDP ranged from 83 to 92 %, indicating DRP was a dominant fraction of TDP in most effluent samples. The dominant fraction of DRP (> 90 %) was also observed in the characterization of influent P mixtures (Table 4). Therefore, P concentration in column leachates hereafter will be discussed in

the context of DRP.

Two-way analysis of variance (ANOVA) on the mass of DRP leached showed very significant effects of P load ( $p < 0.001$ ), P source mixtures ( $p < 0.001$ ), and their interaction ( $p < 0.001$ ) (Table 6). The mass of DRP leached from columns treated with the P source mixtures were 10- to 46-fold greater than that of control columns varying in P loads and P source types used (Table 5). The effect of application rate on the mass of DRP leached was significant ( $p < 0.001$ ) showing about 2-fold differences between application rates. The leachability (mass of P leached / total P applied  $\times$  100) of various P source mixtures through soil columns had a following order: TSP, dissolved  $\text{KH}_2\text{PO}_4$  > dairy liquid = swine liquid > poultry compost = poultry litter = swine sludge ( $p < 0.05$ ). Results suggest that inorganic P sources and liquid wastes would have a greater leaching potential than solid and semi-solid wastes when these P source materials are surface-applied on a total P basis.

The relationship between initial mass of DRP in P mixtures and the mass of DRP leached is shown in Figure 3. The initial mass of DRP in the P mixtures was significantly correlated with the mass of DRP leached ( $r^2 = 0.87$ ), suggesting that dissolved P in source materials is indicative of dissolved P loss through leaching. Similar results were reported in Sharpley and Moyer (2000) who found that water extractable P in manures was very well correlated with cumulative loss of P leached ( $r^2 = 0.98$ ). It is notable that the mass

recovery of DRP from organic P source-treated columns was close to 100% or greater, while that from inorganic P source was less than 100% (see the dashed line in Figure 3). This result indicates that (i) organic P source mixtures in our study released more P than that estimated by the water extraction presumably due to a continuous release of P from solid phase that remained on the soil surface and (ii) dissolved P from the inorganic P source-treated columns was perhaps held tighter than that from organic P source-treated columns.

### **Phosphorus leached over time**

To examine P leaching pattern in the course of leaching, cumulative mass of DRP leached was plotted as a function of PV (Figure 4). Overall variation of cumulative mass of DRP leached showed three distinct phases in a curvilinear shape: slow leaching at earlier stage, faster leaching at intermediate state, and back to slow leaching at final stage (identified as a slope of curves in Figure 4). This phenomenon may be inversely interpreted as P retention in soils with two distinct phases: fast retention at first followed by continuous slow retention (Beck et al., 1998). Exception was the swine sludge treated columns that had not reached a plateau in the curve even after 23 PV of leaching. At the same pulse duration group of 2 PV, TSP started to breakthrough about 1 PV, which was earlier than PC (3 PV), PL (3 PV) and SS (3.5 PV). In the liquid P source mixtures (pulse



duration of 6.8 – 6.92 PV), KP showed earlier breakthrough (2 PV) than DL (5 PV) and SL (5 PV). Similar breakthrough patterns among P mixtures were observed in low P load with a slight delay of P breakthrough. These results demonstrate that the stronger P source strength, the earlier P breakthrough occurs.

### **Concurrent discharge of DRP and DOC**

We examined the concurrent discharge of DRP and DOC in the course of experiment in high P load (Figure 5). From the columns treated with organic P source mixtures (DL, SL, PC and PL), DOC appeared to breakthrough earlier than DRP. The peaks of DOC concentration coincided with breakthrough of DRP, after which DOC showed a sharp decline followed by a slow and continuous decline. This pattern implies that P tends to be retained longer than DOC and thereby more affinity of P to the soil matrix than DOC.

### **Parameter estimation for phosphorus sorption and retardation factor**

Batch P sorption data were fitted with both the Langmuir and the Freundlich isotherm model to determine which model is appropriate for the sorption parameter estimation. Since the Langmuir model has an advantage over the Freundlich in that it provides the information on the P sorption maximum (b) and a constant  $K_L$ , related to the

P bonding (Gratez and Nair, 2000), we chose the Langmuir model to estimate the sorption parameters. The equilibrium P concentration at net zero sorption ( $EPC_0$ ) was  $0.65 \text{ mg L}^{-1}$  and the amount of initial sorbed P in the soil was  $10.1 \text{ mg P kg}^{-1}$ . The ability of the soil to resist a change in the P concentration of the solution phase (PEBC, P equilibrium buffering capacity) was  $15.6 \text{ L kg}^{-1}$ , which is within the typical range of PEBC of fertilized soil (Sui and Thomson, 2000; Mamo et al., 2005). The P sorption maximum ( $S_{\max}$ ) estimated from Eq. [5] was  $318 \text{ mg P kg}^{-1}$  and a constant related to the P bonding energy was  $0.023 \text{ L mg}^{-1}$ .

The sorption partition coefficient ( $k_d$ ) and retardation factor ( $R_L$ ) corresponding to the DRP concentrations of P source mixtures are provided in Table 7. The  $R_L$  ranged from 2.1 to 18.4, indicating that source-derived DRP could be retarded more than Br ( $R = 1.19$ ). The TSP mixture with the highest P source strength ( $200 \text{ mg DRP L}^{-1}$ ) yielded the smallest  $R_L$  (2.1 at high P load and 4.1 at medium P load) while the lowest  $R_L$  was found in SL (18.4 at both P load). This result suggests that the retardation of source-derived P to the soil sorption sites can be inversely related to the P source strength in the mixtures, assuming there is no interaction between adsorbate molecules (e.g., absence of any competing ion against P sorption).

### **Simulation of phosphorus breakthrough**

One-dimensional transport of P was simulated with the CXTFIT using the estimated  $R_L$  in Table 7 and other transport parameters in Table 3. Assuming a semi-finite column, input data was programmed corresponding to the respective P source strength and pulse duration from the P mixtures used. Data only from liquid P source (KP, DL and SL at high P load) was used since the P mixtures from solid and semi-solid mixtures have a solid-phase of P, which makes it difficult to simulate P transport with the program.

Figure 6 shows the CXTFIT-fitted P breakthrough curves as compared to the observed P breakthrough curves in each of P mixtures. In all P mixtures, we observed an earlier breakthrough of P and higher peaks of P concentration than the CXTFIT-fitted P breakthrough, being pronounced in the columns with DL and SL. Clearly, the predicted P breakthrough curve using the  $R_L$  estimated from batch Langmuir isotherm underestimated DRP transport through the soil matrix. This raises questions about the presence of preferential flow in the course of the experiment. Surface-applied P was, however, unlikely to move by preferential flow in our columns due to the symmetrical Br breakthrough observed in our columns (Figure 2), which indicates the absence of preferential flow. The earlier breakthrough of P in liquid wastes is maybe attributable to that DOC competed with P (either from the waste or native soil P) for sorption sites, enhancing P transport through soil matrix. Moreover, organic residues remained on the

surface after the addition of DL and SL was likely to release P slowly via the mineralization of organic P, yielding the long-tailing in their BTC.

## CONCLUSIONS

Surface-applied P from various organic and inorganic sources led to differences in the mass of DRP discharged from the packed columns with loamy sand soil. Within P source mixtures, the columns treated with inorganic P mixtures showed about two-fold greater mass loss of DRP compared to those with organic P mixtures when these P mixtures were surface-applied based on total P basis. The mass loss of DRP was a function of water extractable P in the influent P mixtures ( $r^2 = 0.87$ ), suggesting that the WEP in the P source materials can be a predictive measurement for the P leaching loss.

With a 23 PV of leached water, we demonstrated the source-derived P displacement through soil matrix in various P source materials. Generally the P leaching pattern was consistent with common P retention process in soils characterized by fast retention in the early stage followed by continuous slow retention. Concurrent discharge of source-derived DRP and DOC in the columns treated with organic P sources showed that DOC displaced first followed by P displacement, emphasizing the greater affinity of DRP over DOC in the soil.

The  $R_L$  of P in the study soil estimated from the Langmuir model confirms that the reactive solute (P) had 2- to 20-fold greater  $R_L$  than a conservative tracer (Br), being affected by P concentration in the influent mixtures. We extrapolated the  $R_L$  to predict an ideal one-dimensional transport of P but the predicted P breakthrough curve did not match well with the observed breakthrough curve. The underestimation of P retardation from the Langmuir model was found especially in the columns treated with liquid wastes, indicating that the presence of DOC in the liquid wastes may lead an early P breakthrough, as DOC competes with P for sorption sites. Moreover, the mineralization of P in surface-applied liquid wastes may lead enhanced P breakthrough compared to the predicted P breakthrough. We used a chemical equilibrium-based model in present study, but a chemical non-equilibrium-based model might be better predict P transport in agricultural soils.

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**Table 1. Soil characteristics of Autryville soil.**

Sand	Silt	Clay	OM <sup>†</sup>	pH <sub>H2O</sub> <sup>‡</sup>	P <sub>M3</sub> <sup>§</sup>	P <sub>ox</sub> <sup>¶</sup>	Al <sub>ox</sub> <sup>¶</sup>	Fe <sub>ox</sub> <sup>¶</sup>	DPS <sub>ox</sub> <sup>#</sup>
	%		g kg <sup>-1</sup>			mg kg <sup>-1</sup>			%
92.5	5.4	2.1	11.3	4.9	155	164	299	205	70

<sup>†</sup> Organic matter by loss-on-ignition.

<sup>‡</sup> Soil pH at 1:1 water to soil ratio.

<sup>§</sup> Mehlich-3 extractable P.

<sup>#</sup> Degree of P saturation calculated as the molar ratio of  $100 \times (P_{ox} / [Al_{ox} + Fe_{ox}])$ .

**Table 2. Selected properties of organic P source materials.**

P source materials	Dry matter	pH	Total elemental					
			C	N	P	C to N	C to P	N to P
	%			g kg <sup>-1</sup>			g g <sup>-1</sup>	
Dairy lagoon liquid	0.3	7.4	199	88	21	2	9	4
Poultry compost	79.9	6.7	379	34	15	11	25	2
Poultry litter	71.3	5.9	261	35	17	8	15	2
Swine lagoon liquid	0.3	7.4	179	136	27	1	7	5
Swine lagoon sludge	4.6	7.0	273	39	27	7	10	1

**Table 3. The CXTFIT-fitted solute transport parameters using observed Br data.**

Q <sup>†</sup>	$\theta_v$ <sup>‡</sup>	$v$ <sup>§</sup>	R <sup>¶</sup>	D <sup>#</sup>	$\alpha$ <sup>††</sup>	P <sub>c</sub> <sup>‡‡</sup>	r <sup>2</sup> <sup>§§</sup>
cm <sup>3</sup> d <sup>-1</sup>	cm <sup>3</sup> cm <sup>-3</sup>	cm d <sup>-1</sup>		cm <sup>2</sup> d <sup>-1</sup>	cm		
40	0.32	3.94	1.19	2.36	0.60	17	0.99

<sup>†</sup> Flow rate.

<sup>‡</sup> Volumetric water content.

<sup>§</sup> Pore water velocity [ $v = Q / (A \times \theta_v)$ ].

<sup>¶</sup> Retardation factor.

<sup>#</sup> Dispersion coefficient.

<sup>††</sup> Dispersivity ( $\alpha = D / v$ ).

<sup>‡‡</sup> Column Peclet number ( $P_c = vL / D$ ).

<sup>§§</sup> Square of correlation coefficient between observed and fitted Br data.

**Table 4. Properties of P source mixtures.**

P source Mixture†	P load kg TP ha <sup>-1</sup>	Mixture volume mL	Pulse‡ duration	Concentration§				Mass				Total P partitioning¶	
				TP	TDP	DRP	DOC	TP	TDP	DRP	DOC	Dissolved	Solid
				mg L <sup>-1</sup>				mg				%	%
DL	150	692	6.92	68.7	25.9	23.6	235.9	47.6	17.9	16.3	163.3	38	62
PC	(high)	200	2	237.8	66.6	64.7	332.1	47.6	13.3	12.9	66.4	28	72
PL		200	2	237.8	43.0	41.2	307.1	47.6	8.6	8.2	61.4	18	82
SL		692	6.92	68.7	19.1	17.4	130.6	47.6	13.2	12.1	90.3	28	72
SS		200	2	237.8	31.4	26.1	18.6	47.6	6.3	5.2	3.7	13	87
KP		680	6.8	70.0	70.0	68.5	1.8	47.6	47.6	46.6	1.2	100	0
TSP		200	2	237.8	211.6	200.2	3.9	47.6	42.3	40.0	0.8	89	11
DL	75	346	3.46	68.7	25.9	23.6	235.9	23.8	9.0	8.2	81.6	38	62
PC	(medium)	200	2	118.9	43.3	41.8	186.7	23.8	8.7	8.4	37.3	36	64
PL		200	2	118.9	33.6	32.7	163.4	23.8	6.7	6.5	32.7	28	72
SL		346	3.46	68.7	19.1	17.4	130.6	23.8	6.6	6.0	45.2	28	72
SS		200	2	118.9	29.0	24.2	11.8	23.8	5.8	4.8	2.4	24	76
KP		340	3.4	70.0	70.0	68.5	1.8	23.8	23.8	23.3	0.6	100	0
TSP		200	2	118.9	107.6	101.4	2.2	23.8	21.5	20.3	0.4	90	10

† DL, Dairy lagoon liquid; PC, poultry compost; PL, poultry litter; SL, swine lagoon liquid; SS, swine lagoon sludge; KP, dissolved KH<sub>2</sub>PO<sub>4</sub>; TSP, triplesuperphosphate.

‡ Pulse duration calculated as mixture volume / column liquid capacity.

¶ % dissolved in total P partitioning calculated as TDP (mg) / TP (mg) multiplied by 100 and % solid was (100 - % liquid).

§ TP, total P; TDP, total dissolved P; DRP, dissolved reactive P; DOC, dissolved organic carbon.

**Table 5. Phosphorus leached from columns amended with various P source materials at high and medium P load.**

P source mixture	P application rate kg TP ha <sup>-1</sup>	P concentration		Mass leached			Leachability ‡	
		TDP§	DRP¶	TDP§	DRP¶	DRP / TDP	TDP§	DRP¶
		mg L <sup>-1</sup>		mg		%	%	
Unamended	0 (control)	1.7	1.6	0.8	0.7	92	NA#	NA#
Dairy lagoon liquid	150	8.7	7.9	19.6	17.8	91	41	37
Poultry compost	(High load)	7.3	6.3	16.5	14.1	86	35	30
Poultry litter		8.0	6.9	18.3	15.6	86	38	33
Swine lagoon liquid		8.1	7.5	18.2	16.8	92	38	35
Swine lagoon sludge		6.6	6.0	15.0	13.7	91	32	29
Dissolved KH <sub>2</sub> PO <sub>4</sub>		15.8	14.1	35.8	32.0	90	75	67
Triplesuperphosphate		16.1	13.4	36.5	30.3	83	77	64
Dairy lagoon liquid	75	4.8	4.2	10.9	9.6	89	46	41
Poultry compost	(Medium load)	3.6	3.1	8.1	7.0	86	34	29
Poultry litter		4.0	3.5	9.1	7.9	87	38	33
Swine lagoon liquid		5.3	4.8	12.1	10.8	89	51	45
Swine lagoon sludge		3.6	3.3	8.3	7.5	90	35	32
Dissolved KH <sub>2</sub> PO <sub>4</sub>		8.4	7.4	19.2	16.8	88	81	71
Triplesuperphosphate		7.8	6.6	17.6	15.0	85	74	63

† Volume-weighted concentration calculated as (mass of P leached) / (cumulative leachate volume).

‡ Leachability (%) calculated as (mass of P leached) / (total P applied) × 100.

§ Total dissolved P.

¶ Dissolved reactive P.

# Not applicable.

**Table 6. Two-way ANOVA analysis on the mass of DRP leached.**

Variable	DF†	MS‡	F-value	p-value
Load	1	927.62	982.52	<.0001
Source	6	198.43	210.17	<.0001
Source × Load	6	25.04	26.52	<.0001
Error	28	0.94	NA§	NA§

† Degree of freedom

‡ Mean square

§ Not applicable

**Table 7. Estimated retardation factors of source-derived P corresponding to the DRP concentration of P source mixtures from the Langmuir P sorption isotherm.**

P source mixture	High P load (150 kg TP ha <sup>-1</sup> )			Medium P load (75 kg TP ha <sup>-1</sup> )		
	DRP†	k <sub>d</sub> ‡	R <sub>L</sub> §	DRP†	k <sub>d</sub> ‡	R <sub>L</sub> §
	mg L <sup>-1</sup>	L kg <sup>-1</sup>		mg L <sup>-1</sup>	L kg <sup>-1</sup>	
Dairy lagoon liquid	23.6	3.1	15.4	23.6	3.1	15.4
Poultry compost	64.7	1.2	6.5	41.8	1.9	9.9
Poultry litter	41.2	1.9	10.0	32.7	2.4	12.1
Swine lagoon liquid	17.4	3.7	18.4	17.4	3.7	18.4
Swine lagoon sludge	28.1	2.8	14.3	24.2	3.0	15.1
Dissolved KH <sub>2</sub> PO <sub>4</sub>	68.5	1.1	6.2	68.5	1.1	6.2
Triple superphosphate	200.2	0.2	2.1	101.4	0.7	4.1

† Dissolved reactive phosphorus.

‡ Partition coefficient.

§ Retardation factor estimated from the Langmuir isotherm.

		<u>Factor A, P load (kg P ha<sup>-1</sup>)</u>					
		150 (high)			75 (Medium)		
<u>Factor B, P source materials</u>	Dairy lagoon liquid (DL)	●	●	●	●	●	●
	Poultry compost (PC)	●	●	●	●	●	●
	Poultry litter (PL)	●	●	●	●	●	●
	Swine lagoon liquid (SL)	●	●	●	●	●	●
	Swine lagoon sludge (SS)	●	●	●	●	●	●
	Triple superphosphate (TSP)	●	●	●	●	●	●
	Dissolved KH <sub>2</sub> PO <sub>4</sub> (KP)	●	●	●	●	●	●
	No amendment (Control; CN)				●	●	●

**Figure 1. Phosphorus source treatments following two way factorial arrangements on a completely randomized design. Note that each circle symbolizes a column.**

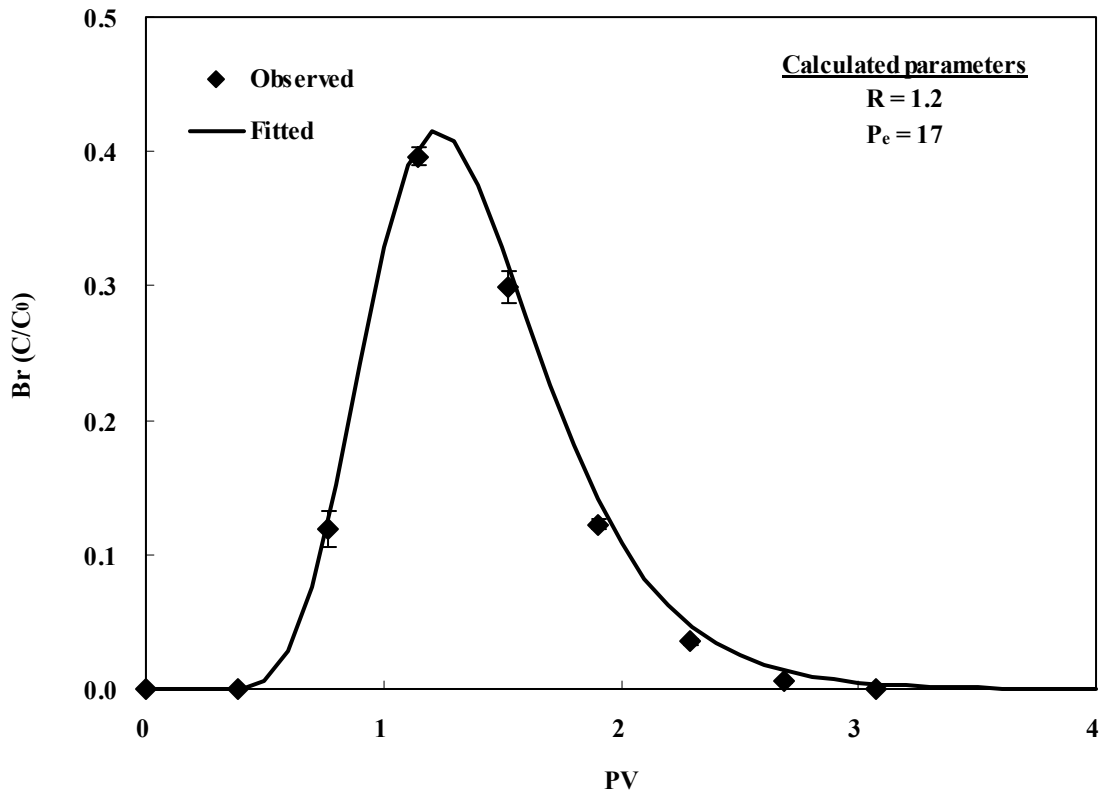
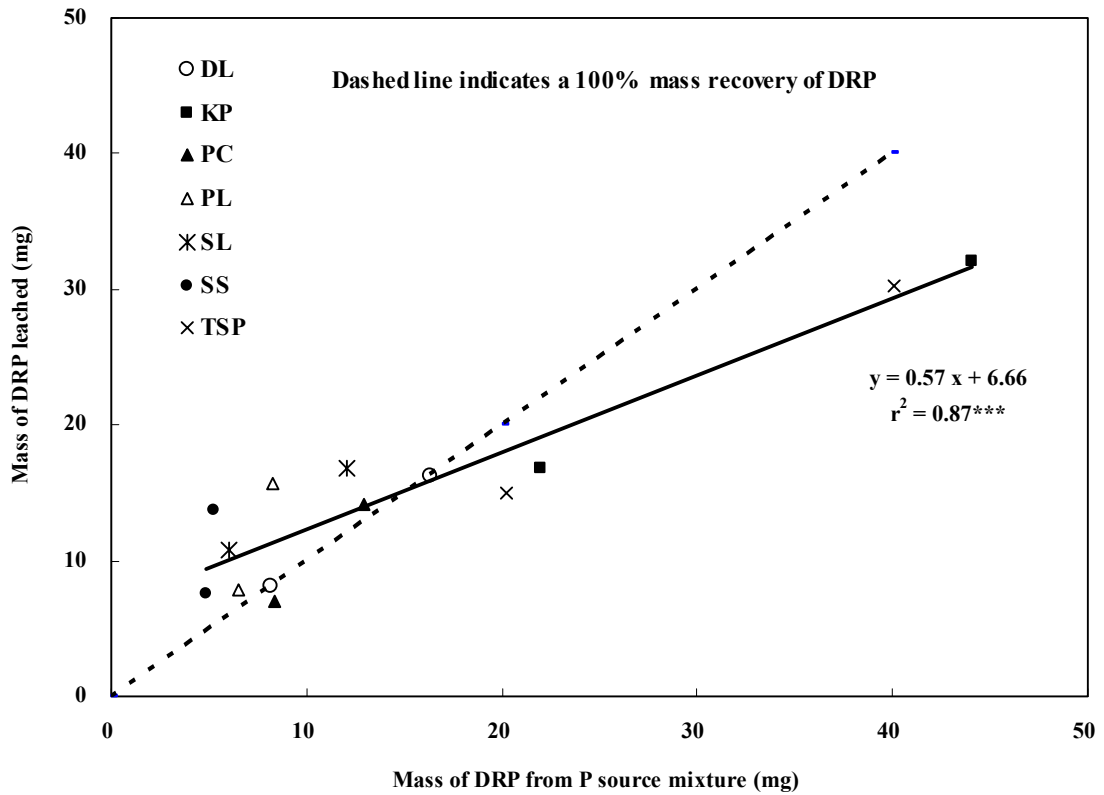
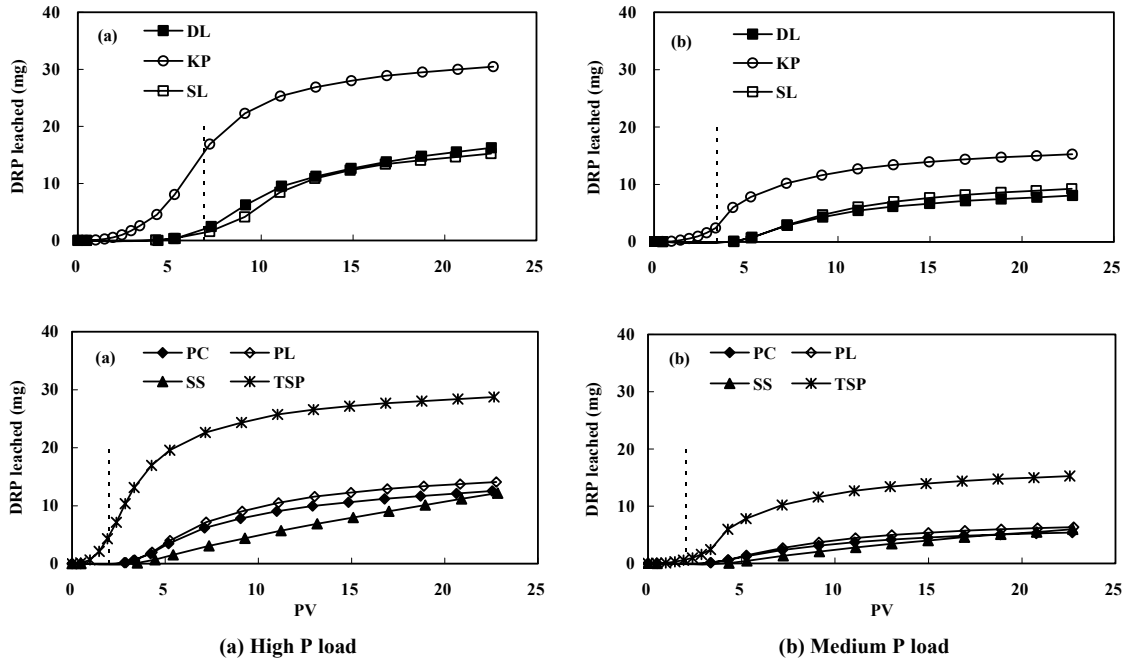


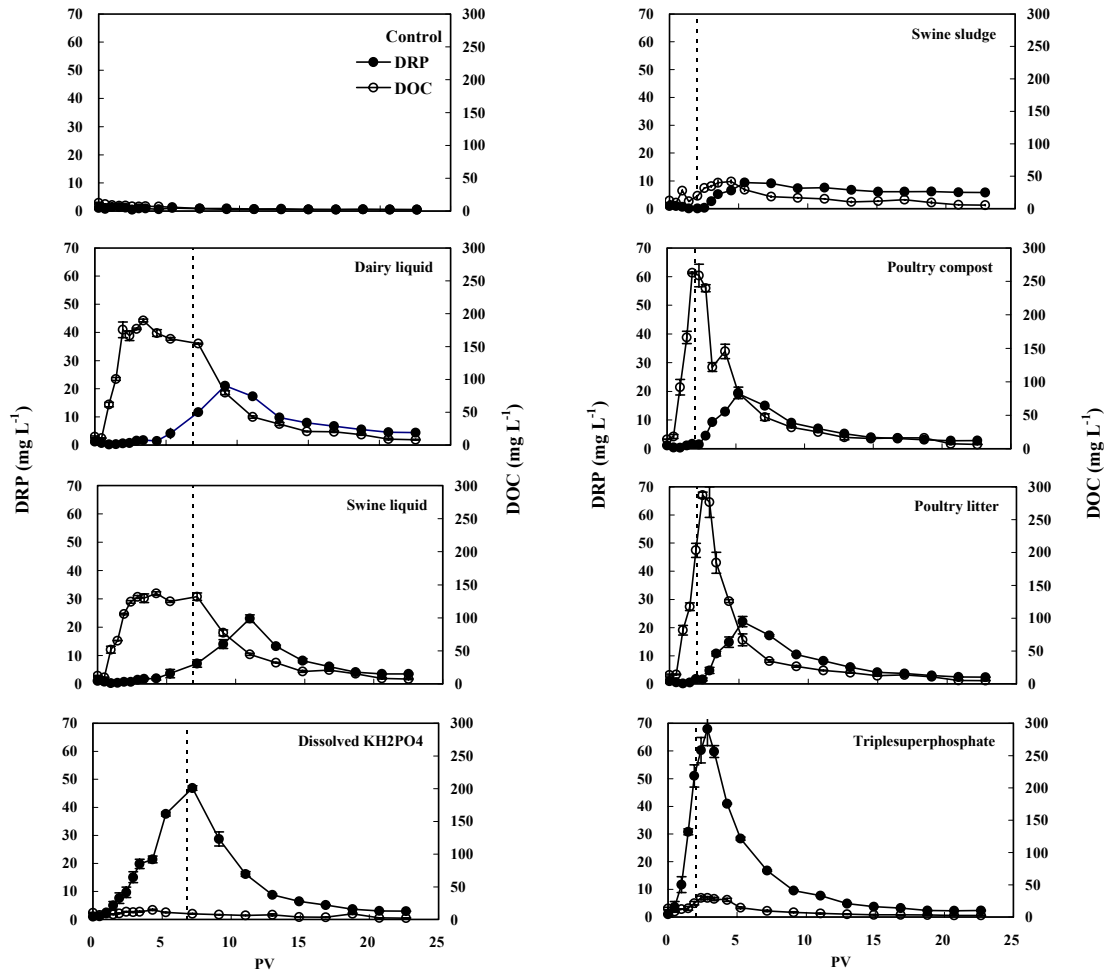
Figure 2. Bromide (Br) breakthrough curve fitted with the CXTIFT. Bars indicate standard errors of the mean from all 45 columns.



**Figure 3. Relationship between the mass of DRP in influent P mixtures and the mass of DRP leached (DL; dairy liquid, KP;  $\text{KH}_2\text{PO}_4$ , PC; poultry compost, PL; poultry litter, SL; swine liquid, SS; swine sludge, and TSP; triplesuperphosphate).**

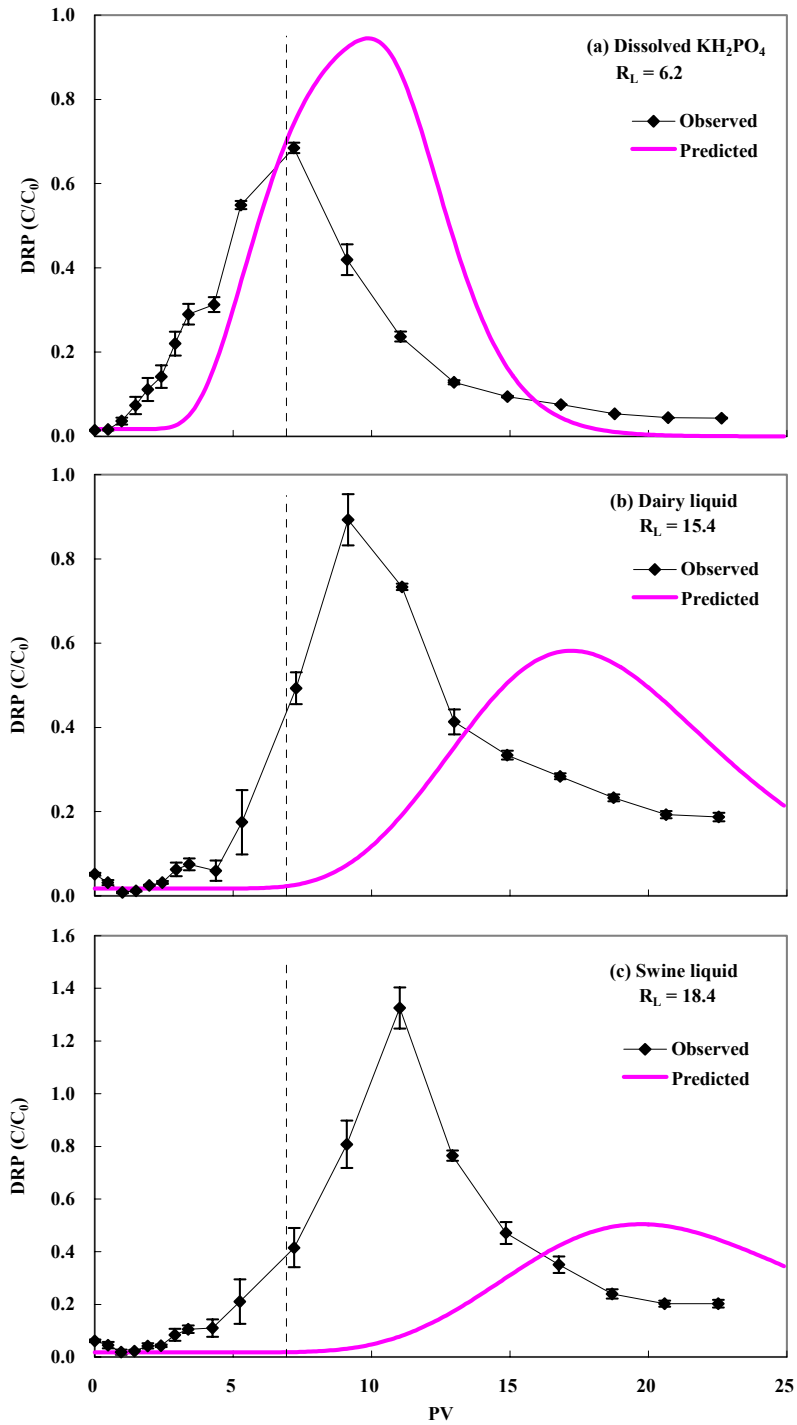


**Figure 4. Cumulative mass of dissolved reactive phosphorus (DRP) leached in (a) high P load and (b) medium P load. Dashed lines show the switching point of P source mixture to deionized water.**



**Figure 5. Concurrent discharge of dissolved reactive P (DRP) and dissolved organic carbon (DOC) in high P load. Dashed lines show the switching point of P source mixture to DI water. Error bars indicates standard error of the mean concentration of DRP and DOC.**





**Figure 6. Comparison of CXTIFT-fitted P breakthrough curve with observed P breakthrough in study columns: dissolved KH<sub>2</sub>PO<sub>4</sub> (C<sub>0</sub> = 68.5 mg P L<sup>-1</sup>), dairy liquid (C<sub>0</sub> = 23.6 mg P L<sup>-1</sup>), and swine liquid (C<sub>0</sub> = 17.4 mg P L<sup>-1</sup>). Error bars indicates standard error of the mean concentration of DRP.**

## CHAPTER 3

### Manure-Derived Organic Carbon in Controlling Phosphorus Sorption

#### INTRODUCTION

In areas of intensive animal agriculture, land application of animal wastes has been employed as a waste disposal alternative (Pautler and Sims, 2000). Continuous land application of animal wastes to meet crop N needs often resulted in the elevated concentrations of soil P (Sharpley et al., 2002; Zhang et al., 2005). Elevated concentrations of soil P has been related to accelerated eutrophication in surface waters (Daniel et al, 1998; Sharpley et al., 1999).

Organic P content in animal wastes varies with animal species, age and diet, but typically ranges from 5 to 25 % of total P (Sharpley and Moyer, 2000). The principal components of organic P in animal wastes are inositol hexaphosphates (IP<sub>6</sub>), nucleic acids, and phospholipids (Baxter et al., 2003). Organic phosphorus has been reported to have greater affinity for sorption than inorganic P (McKercher and Anderson, 1989; Leytem et al., 2002; Berg and Joern, 2006). For example, Leytem et al. (2002) determined the Langmuir P sorption maximum ( $S_{\max}$ ) of inorganic P (Pi), adenosine 5'-triphosphate (ATP), and IP<sub>6</sub> of a sand, sandy loam, and sandy clay loam, and they found that the  $S_{\max}$  followed the order of  $Pi < ATP < IP_6$ . The preferential sorption of organic P over

inorganic P has been also found to cause desorption of Pi from soil P in the presence of organic P compounds, resulting in a net decrease in total P sorption (Berg and Joern, 2006).

Land application of animal wastes also plays an important role in replenishing carbon (C) to the soil system. The levels of both total organic carbon and dissolved organic carbon (DOC) are influenced by the types of animal waste applied (Ohno et al., 2005). The DOC in animal wastes can influence several chemical processes due to its reactivity with both soil solution and soil surfaces through chemical processes such as ligand exchange, hydrophobic interaction and bridging with metal ions on the soil colloid surfaces (Sposito, 1989). Competitive sorption of low molecular weight organic acids (LOAs) with P for sorption sites in soils has been reported to increase dissolved P concentration in the soil solution and thereby decrease a net P sorption (Bolan et al., 1994; Iyamuremye et al., 1996; Bhatti et al., 1998). Metal complexation by organic acids at mineral surfaces and subsequent dissolution of P associated with metal ions has been found to increase P concentration in soil solution (Traina et al. 1987; Fox and Comerford, 1992). In addition, sorption of DOC may increase the negative charge on the soil surfaces, thus inhibiting P sorption (Jiao et al., 2007). In contrast, the formation of metal bridges between OM and metal cation on the colloidal surfaces may increase the sorption of P by creating more P sorption sites (Appelt et al, 1975; Guppy et al., 2005).

Past studies have often used the synthetic or simple dissolved C compounds in evaluating the interaction between DOC and P in soil system. Our study was designed to investigate the role of manure-derived DOC in affecting manure-derived P sorption. Batch sorption experiments using aqueous manure extracts as equilibrating solutions were conducted with a sandy loam. Specific objectives of this study were (i) to examine competitive sorption between manure-derived DOC and P and (ii) to investigate the ability of manure-derived DOC as an organic complexing agent.

## **MATERIALS AND METHODS**

### **Soil materials**

A surface horizon (0-30 cm) of an Autryville soil (Loamy, siliceous, subactive, thermic Arenic Paleudults) was collected from a farm in Sampson County, NC. The soil was air-dried and ground to pass a 2-mm sieve. The soil was 92.5% sand, 5.4% silt and 2.1% clay with a pH of 4.9 (Table 1). The soil had a 155.5 mg kg<sup>-1</sup> of Mehlich-3 extractable P ( $P_{M3}$ ) and degree of P saturation ( $DPS_{ox}$ ) calculated as the molar ratio of P to Al and Fe by oxalate extraction was 70%, indicating overfertilization of P in this soil.

### **Aqueous manure extracts**

We used poultry litter (PL) and swine lagoon sludge (SS) to obtain aqueous extracts. The manure materials were extracted at 20:1 (v/m) deionized water / manure ratio for 24-h on a reciprocating shaker at 120 cycles per minute (cpm). Suspensions were centrifuged at  $10,000 \times g$  for 10 min, and filtered through a 0.2- $\mu\text{m}$  membrane. The filtered extracts were measured for total concentration of P, Al, Fe, Ca and Mg by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The DOC in the extracts was measured by the Shimadzu carbon analyzer (Shimadzu Corp., Tokyo). Selected properties of the aqueous manure extracts are provided in Table 2.

Total acidity and amount of carboxylic group in the raw PL and SS were determined by titration according to the method of Schnitzer (1982). The amount of phenolic hydroxyl groups were ascribed to the difference between total acidity and carboxylic groups (Table 3).

### **Sorption experiment**

The original manure extracts were diluted with  $\text{CO}_2$ -free deionized (DI) water by 2, 4, 10, 20, 50 and 100 times to have various ranges of DOC and P in the equilibrating solutions. Dissolved  $\text{KH}_2\text{PO}_4$  ( $100 \text{ mg P L}^{-1}$ ) and dissolved citric acid ( $500 \text{ mg DOC L}^{-1}$ ) were also prepared as equilibrating solutions to represent synthetic sources of P and DOC.

The same dilution procedures were used for these synthetic sources.

Four parallel series of sorption experiment corresponding to different equilibrating solutions (PL extract, SS extract, dissolved  $\text{KH}_2\text{PO}_4$ , and citric acid) were determined by reacting one gram of soil with 30 mL of equilibrating solution in a 40-mL centrifuge tube. The phosphorus additions ranged from 0 to 1600 mg P  $\text{kg}^{-1}$  while the DOC additions were from 0 to 5000 mg  $\text{L}^{-1}$ . The samples were shaken for 42-h in a thermostat shaker bath ( $20 \pm 1^\circ\text{C}$ ) at 120 cycles per minute (cpm). To minimize the pH effect on the sorption of P and DOC, we checked and adjusted the pH of suspensions to  $6.0 \pm 0.5$  after 8-h and 32-h equilibration under  $\text{CO}_2$ -free condition. Blanks without soil were used to check that no previous association occurs between P and DOC during the period of equilibration.

The Freundlich equation was used to describe sorption of P by:

$$S = K_f C^{1/n} \quad [1]$$

where  $S$  is the amount of P sorbed ( $\text{mg kg}^{-1}$ ),  $K_f$  is the adsorption constant ( $\text{mg kg}^{-1}$ ),  $C$  is the P concentration in solution after equilibration ( $\text{mg L}^{-1}$ ), and  $n$  is a correction factor. By plotting the linear form of Eq. [1],  $\log S = \log K_f + 1/n \log C$ , the slope is the value of  $1/n$  and the intercept is equal to  $\log K$ .

Initial mass (IM) sorption isotherm was used to describe sorption of DOC in the soil (Nodvin, 1986). The amount of DOC sorbed or released is plotted as a function of the

initial concentration of DOC by:

$$RE = m X_i - b \quad [2]$$

where RE is the amount of DOC or P released or sorbed ( $\text{mg kg}^{-1}$ ),  $X_i$  is the amount of DOC added ( $\text{mg kg}^{-1}$ ) and  $m$  is the slope of the linear regression. The intercept of the linear regression,  $b$ , indicates the amount of DOC or P released when  $X_i = 0$ . The IM isotherm distribution coefficient ( $K_d$ ) was calculated from the slope of the IM isotherm as in Eq. [3] and can be a measure of the affinity of DOC for the soil (Donald et al, 1993).

$$K_d = \frac{1 - m}{m} \times \frac{\text{volume of soil}}{\text{soil mass}} \quad [3]$$

## RESULTS AND DISCUSSION

### Sorption of dissolved phosphorus

Figure 1 shows the Freundlich P sorption isotherms segmented by the types of equilibrating solutions (PL and SS extracts as compared to the dissolved KP). The  $K_f$  for SS ( $8.98 \text{ mg kg}^{-1}$ ) was greater than those for  $\text{KH}_2\text{PO}_4$  ( $8.66 \text{ mg kg}^{-1}$ ) and PL ( $8.78 \text{ mg kg}^{-1}$ ), showing a greater P sorption with SS (Table 4). This result is in agreement with Ohno and Crannell (1996) who found that the presence of DOC extracted by cattle and poultry manure extracts increased P sorption, while vetch and clover extracts, as well as citric acid, inhibited P sorption. Our result in combination with Ohno and Crannell (1996)

implies that the DOC extracted from animal wastes (PL and SS) may behave differently with that from plant residues in affecting P sorption in soils. However, this implication is only limited to controlled batch experiment with a relative short-time of equilibration (<48-h) which permits a minimal P and C mineralization.

### **Sorption of dissolved organic carbon**

Figure 2 shows linear IM isotherms for DOC, segmented by the types of equilibrating solutions (PL and SS extracts as compared to the dissolved citric acid). The differences in the DOC sorption between the DOC source types were pronounced, which can be identified as the slope ( $m$ ) of the IM isotherms. The slope for CA ( $m = 0.25$ ) was two-fold greater than that of SS ( $m = 0.12$ ) and six-fold greater than that of PL ( $m = 0.04$ ). The differences in the slopes resulted in greater  $K_d$  for CA ( $4.96 \text{ mg kg}^{-1}$ ) than SS ( $1.95 \text{ mg kg}^{-1}$ ) and PL ( $0.55 \text{ mg kg}^{-1}$ ) as in Table 4. The greater sorption of DOC in CA could be due to either a stronger bonding affinity or to lack of competition from P. The presence of P in the PL and SS extracts was likely to compete with manure-derived DOC for the sorption sites, decreasing the amount of DOC sorbed. This result is similar with Kaiser and Zech (1997) who reported that the presence of phosphate in the soil solution induced a strong decrease in dissolved organic matter (DOM) sorption. The lower sorbed DOC from PL than SS may be attributable to the difference in COOH groups of respective



materials (Table 2). The SS ( $0.90 \text{ mmol g}^{-1}$ ) had a two-fold greater COOH than the PL ( $0.49 \text{ mmol g}^{-1}$ ), which indicates that the organic acids in SS are more humified than those in PL (Unsal and Ok, 2001).

### **Role of manure-derived dissolved organic carbon on phosphorus sorption**

The ability of LOAs to release inorganic anions, such as P, from mineral surfaces is well documented and has been attributable to complex formation between organic acids and metal ions (e.g., Al and Fe) and subsequent release of P associated with these mineral oxides (Traina et al., 1985; Bhatti et al., 1998). Bolan et al. (1994) demonstrated that increasing carboxylic groups in soil solution can increase P release from soil minerals (tri-carboxylic acid > di-carboxylic acid > mono-carboxylic acid). This preference for di- and tri-carboxylic acids groups reflects the greater stability constant for complexes with Al and Fe in solution or colloid surfaces and their increased capacity to form bidentate ligand exchange bonds (Guppy et al., 2005). Moreover, organic acids capable of forming stable aqueous complexes with Al and Fe in soil solution can increase P concentration in solution, decreasing overall P sorption (Fox and Comerford, 1992).

Figure 4 shows the relationship between DOC sorbed and P desorbed from the study soil when only citrate was used as an equilibrating solution. We observed an increase in dissolved P concentration with increasing input of citrate, which likely

resulted from a ligand exchange reaction of citrate acid, replacing  $\text{PO}_4$  on soil mineral surfaces (Bhatti et al., 1998). Clearly, citric acid, a tri-carboxylic acid, appeared to be a strong organic complexing agent that can replace P sorbed on soil mineral surfaces. In the light of the results from citrate, we questioned the ability of manure-derived DOC as an organic complexing agent. Based on our results of decreased DOC sorption from the manure extracts as compared to citrate, organic acids in the manure extracts behave like mono-carboxylic acids, which is indicated by relatively low fraction of carboxylic groups in proportion to total acidity (Table 2, 0.07 for PL and 0.17 for SS).

We observed a slight increase in P sorption with the SS extract compared to the P sorption with dissolved  $\text{KH}_2\text{PO}_4$  (Figure 1). We suspect that formation of metal bridges between DOC and mineral oxides of Al, Fe and Ca may have resulted in the increased P sorption with the SS extract, opening further surfaces on which fresh P sorption occurs (Guppy et al., 2005). Inhibition of P sorption by competitive sorption between DOC and P to sorption sites was likely to be offset by the formation of soluble complexes that can eventually result in new sorption sites on the mineral surfaces (Appelt et al., 1975).

Under batch sorption conditions of this study, manure-derived P sorbed with greater affinity than inorganic P (dissolved  $\text{KH}_2\text{PO}_4$ ) in the study soil. This contradicts the results of Chapter 2 that there was a DOC-enhanced P transport in the soil columns treated with liquid wastes as compared to the soil columns treated with dissolved

$\text{KH}_2\text{PO}_4$ . The DOC-enhanced P transport in Chapter 2 may be explained by the mineralization of organic P from the applied liquid wastes in the course of experiment (50-d) rather than competitive inhibition of P sorption in the presence of DOC. Future research should focus on the long-term effects of OM addition as well as microscopic approach to elucidate the effects of metal bridges between DOC and mineral oxides on the P sorption.

## CONCLUSIONS

Present study evaluated the influence of DOC on P sorption and vice versa using the aqueous extracts of poultry litter and swine sludge along with dissolved  $\text{KH}_2\text{PO}_4$  and citric acid. The presence of manure-derived DOC did not inhibit the sorption manure-derived P in a sandy soil. Instead, manure-derived DOC sorption was inhibited in the presence of manure-derived P as compared to citric acid, suggesting that the DOC from the manure extracts was a less competitive organic complexing agent than citric acid. The competitive sorption of manure-derived DOC versus manure-derived P was minimal in our short-term equilibrium study (42-h). The enhanced P mobility in soils amended with animal wastes may result from the mineralization of organic P from animal wastes rather than competitive inhibition of P sorption in the presence of DOC.

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**Table 1. Selected properties of study soil.**

Sand	Silt	Clay	OM <sup>†</sup>	pH <sub>H2O</sub> <sup>‡</sup>	P <sub>M3</sub> <sup>§</sup>	P <sub>ox</sub> <sup>¶</sup>	Al <sub>ox</sub> <sup>¶</sup>	Fe <sub>ox</sub> <sup>¶</sup>	DPS <sub>ox</sub> <sup>#</sup>
	%		g kg <sup>-1</sup>			mg kg <sup>-1</sup>			%
92.5	5.4	2.1	11.3	4.9	155	164	299	205	70

<sup>†</sup> Organic matter by loss-on-ignition.

<sup>‡</sup> Soil pH at 1:1 water to soil ratio.

<sup>§</sup> Mehlich-3 extractable P.

<sup>#</sup> Degree of P saturation calculated as the molar ratio of  $100 \times (P_{ox} / [Al_{ox} + Fe_{ox}])$ .

**Table 2. Chemical properties of the aqueous extracts from poultry litter and swine lagoon sludge.**

Manure extracts	pH	DOC <sup>†</sup>	P	Al	Fe	Ca	Mg	S	P/DOC
					mg L <sup>-1</sup>				mg mg <sup>-1</sup>
Poultry litter	8.3	538	108	0.09	1.33	29.5	9.3	0.0	0.20
Swine sludge	7.2	80	67	< 0.05 <sup>‡</sup>	< 0.05 <sup>‡</sup>	38.8	24.7	0.0	0.84

<sup>†</sup> Dissolved organic carbon.

<sup>‡</sup> Values below detection limit.

**Table 3. Surface functional groups of poultry litter and swine sludge.**

Source	Total surface acidity	Carboxylic (-COOH) groups	Phenolic(-OH) groups	COOH/total acidity
		mmol g <sup>-1</sup>		mmol mmol <sup>-1</sup>
Poultry litter	7.04	0.46	6.58	0.07
Swine sludge	5.42	0.90	4.52	0.17

**Table 4. Sorption parameters for P and DOC in Autryville soil.**

Freundlich isotherm for P			IM isotherm for DOC		
Source	n†	K <sub>f</sub> ‡	Source	m§	K <sub>d</sub> ¶
		mg kg <sup>-1</sup>			mg kg <sup>-1</sup>
KH <sub>2</sub> PO <sub>4</sub>	1.81	8.66	Citric acid	0.25	4.96
Poultry litter	1.81	8.78	Poultry litter	0.04	0.55
Swine sludge	1.64	8.98	Swine sludge	0.12	1.95

† Correction factor.

‡ Adsorption constant of P.

§ Slope of IM isotherm.

¶ Distribution coefficient of DOC.

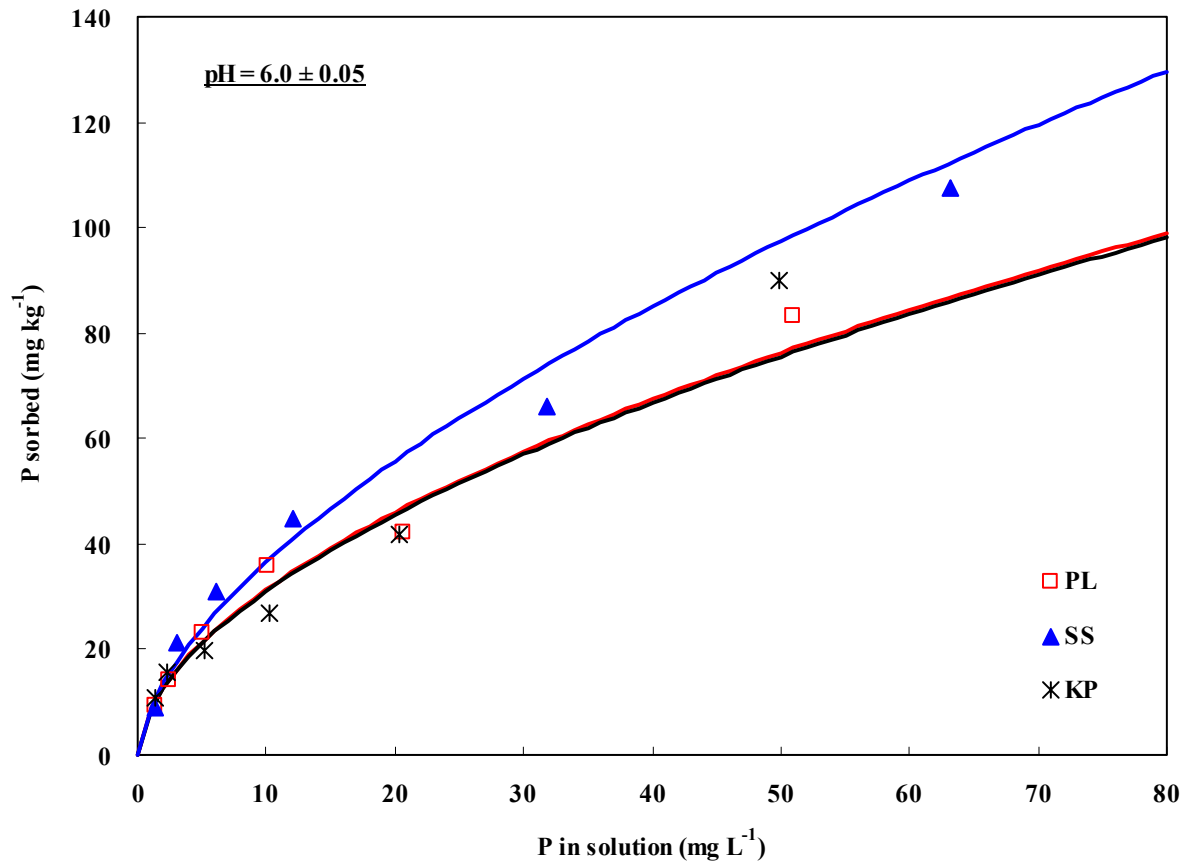
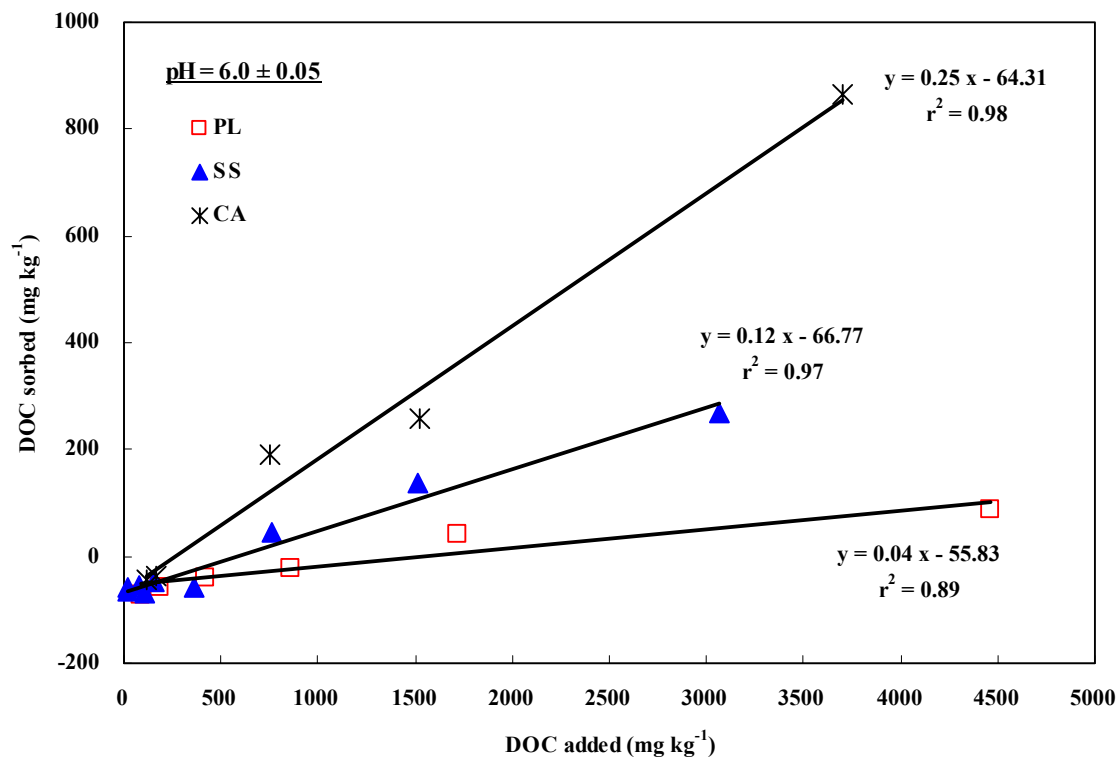


Figure 1. Freundlich sorption isotherms for phosphorus in Autryville soil equilibrated with poultry litter (PL), swine sludge (SS) and dissolved  $\text{KH}_2\text{PO}_4$  (KP).





**Figure 2. Initial mass isotherm for dissolved organic carbon in Autryville soil equilibrated with poultry litter (PL) extract, swine sludge (SS) extract and dissolved citric acid (CA).**

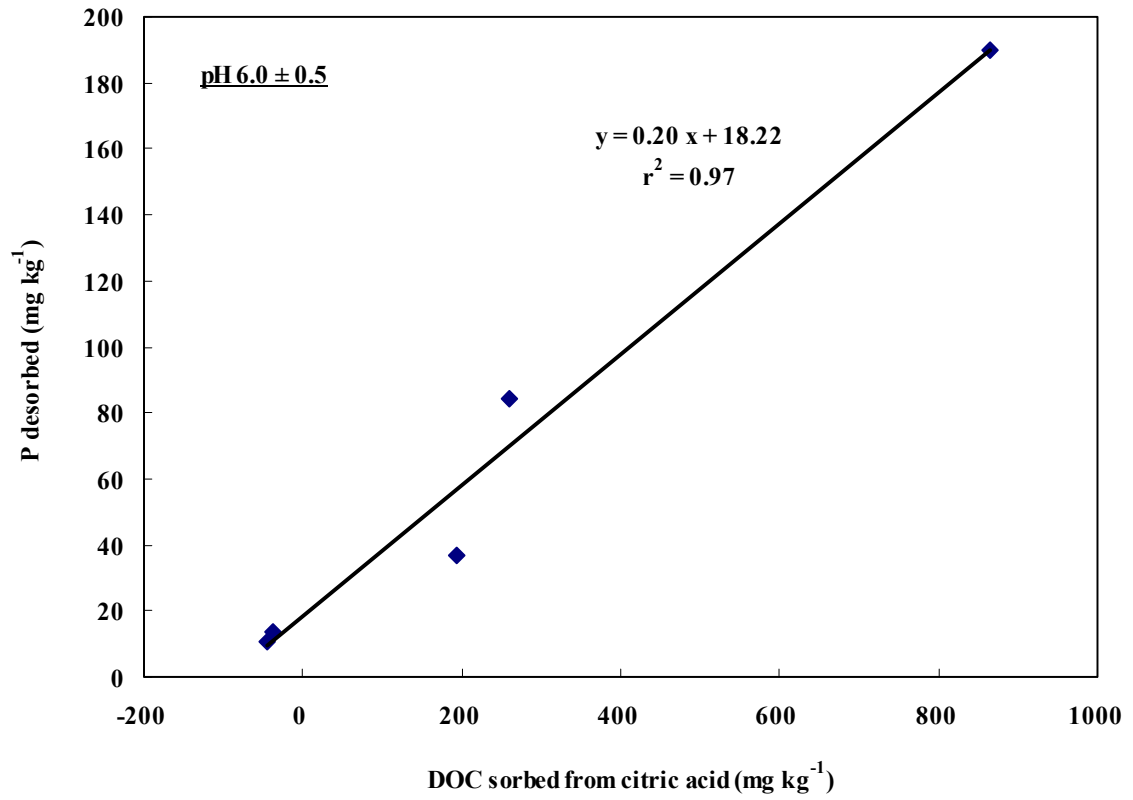


Figure 3. Comparison of DOC sorbed with P desorbed in Autryville soil when equilibrated with citrate citric acid.

## CHAPTER 4

### Deep Leaching of Phosphorus in the Coastal Plain Soils of North Carolina

#### INTRODUCTION

Phosphorus (P) usually shows limited mobility in soils and its contribution to accelerated water eutrophication is mostly attributable to surface flow rather than subsurface flow (Sims et al., 1998; Elliot et al., 2002). However, areas of intensive animal agriculture of the Atlantic Coastal Plain of North Carolina (NC) can be susceptible to deep leaching of P due to a long history of overfertilization (Ham, 1999; Novak et al., 2000; Nelson et al., 2005). For example, Novak et al (2000) observed a Mehlich-3 P ( $P_{M3}$ ) concentration of  $151 \text{ mg P kg}^{-1}$  at a depth of 100 cm in the fields that had received swine liquid for 10 years. In the literature, significant P leaching has been reported in heavily-fertilized sandy soils and organic-rich soils with low P sorption capacity, and fine-textured soils with preferential flow (Eghball et al., 1986; Sims et al., 1998; Nelson et al., 2005). In addition, artificial drainage systems (tiles and ditches) in agricultural fields are known to accelerate downward movement of dissolved P that would normally percolate slowly through the soil matrix (Dils and Heathwaite, 1996; Sims et al, 1998; Beauchemin et al., 2003).

Release of P to percolating waters may depend on soil P concentration, P sorption

capacity, transport pathways, and hydraulic conditions (Godlinski et al., 2004). Positive correlation has been reported between soil test P (e.g., Mehlich-3 P and Olsen P) and dissolved P of leachate in several studies using intact soil columns or field lysimeters (Heckrath et al., 1995; McDowell and Sharpley, 2001; Siddique and Robinson., 2003; McDowell and Sharpley, 2004).

Degree of P saturation (DPS) of soils, calculated as a single extraction of ammonium oxalate ( $DPS_{ox}$ ) in the dark (pH 3), has been suggested as an indicator for the risk of P loss via leaching and subsequent subsurface lateral flow (Hooda et al., 2000; Maguire and Sims, 2002; Butler and Coale, 2005). It has been shown that only small amounts of P are weakly bound in soils below a certain DPS threshold, but weakly bound P increases rapidly above this threshold (Pautler and Sims, 2000; Nair et al. 2004). However, these relationships have been mostly established for shallow leaching of P (a depth of <30 cm) and deep leaching of P has not been thoroughly investigated. Surface soil P concentrations might be indicative of potential P release, but subsoil properties, including P status, might have stronger influence on the deep leaching of P (Djordjic et al., 2004; Nelson et al., 2005). Moreover, most P leaching studies have used well-drained mineral soils with low OM so that it is difficult to compare P leaching potentials in soils varying in organic matter concentration. The OM concentration in soils is as important factor as  $DPS_{ox}$  in predicting deep leaching of P (Godlinski et al., 2004). Clearly, P

leaching from organic-rich soils needs more attention due to the unique P sorption characteristics from these soils.

Controlled drainage by water control structures is a best management practice for managing water tables in the Tidewater region of NC (Osmond et al., 2002). When obstructive boards are inserted into the drain outlet of a water control structure, the drainage intensity decreases and any excessive rainfall will cause the water table level in the field to rise up and to be maintained at a controlled level. The recommended level of the water control structure (depth below average surface elevation at the outlet) during the fallow season in NC is 30- to 46-cm deep to minimize drainage outflow and encourage denitrification (Evans et al., 1991). As a result, a larger part of the subsoil is submerged, promoting denitrification and reducing nitrate loss in drainage outflow by 20 % (Evans et al., 1991). Even though the decreased nitrate loss in controlled drainage is well-documented, the P behavior in controlled drainage is in question due to the possibility of increased soluble P concentration that may occur through reductive dissolution of Fe(III) compounds associated with phosphorus (Vadas and Sims, 1998; Hutchison and Hesterberg, 2004). Since controlled drainage usually creates water-saturated subsoils, the P behavior in the saturated subsoils is likely to be different with that of flooded soils where saturation occurs near the soil surface.

Here we present the results of a deep P leaching study conducted with intact soil

columns collected from the Coastal Plain soils of NC where P leaching loss can be potentially significant due to shallow water table and artificial drainage system. The objectives of this study were (i) to evaluate the influence of Mehlich-3 P concentration in surface soil and subsoil on the P leaching, (ii) to compare P leaching potentials between well-drained mineral soils and poorly drained organic-rich soils and (iii) to examine the effects of subsoil saturation on the P leaching.

## **MATERIALS AND METHODS**

### **Soil columns**

Intact soil columns (6.5-cm diameter and 90-cm long) were collected from twelve sites that were dominated by one of four soil series in the Coastal Plain of NC: Autryville (Loamy, siliceous, subactive, thermic Arenic Paleudults), Goldsboro (Fine-loamy, siliceous, subactive, thermic Aquic Paleudults), Cape Fear (Fine, mixed, semiactive, thermic Typic Umbraquults), and Wasda (Fine-loamy, mixed, semiactive, acid, thermic Histic Humaquepts). Autryville and Goldsboro are well-drained mineral soils while Cape Fear and Wasda are poorly-drained mineral-organic soils (Table 1). For each soil, three sites that had received P from one of three P sources (triplesuperphosphate (TSP), poultry litter (PL), and swine lagoon liquid (SL)) were

selected and 4 replicated columns per site were removed with a hydraulic soil sampling unit (Giddings probe) equipped with a 6.5-cm diameter steel tube containing a polyethylene terephthalate copolymer (PTEG) liner. Target column length was 90 cm but it varied from 75 to 97 cm (mean length = 90 cm) due to the difficulties of intact column removal (e.g., dry sandy subsoils or wet clayey subsoils). To collect column leachate, the bottom of the soil column was sealed to a funnel where multiple layers of cheese cloth were placed between the bottom of the column and the funnel. A total of 72 columns were placed in a lab, prewet by adding excess deionized (DI) water and left to drain to field capacity for 2-d.

### **Phosphorus source addition**

To prevent a confounding effect of P source type between field and lab, soil columns collected from historical applications of TSP, PL, and SS received the same type of P source treatment in the laboratory condition. We defined a simulated year as a period of 12 weeks and we surface-applied the P source materials every 12 week at a rate of 100 kg total P ha<sup>-1</sup>. We performed the leaching experiment for 48 weeks (4 simulated years) and soil columns received the equivalent amount of 400 kg ha<sup>-1</sup> of total P. TSP and PL were applied at the beginning of every 12 week period, while SL was irrigated weekly at 8.33 kg P ha<sup>-1</sup> to accommodate the proposed P rate. Deionized (DI) water was applied to

the top of columns at a rate of 2.7-cm (90mL) / wk. The columns treated with SL received an addition of 12.4-cm of effluent (412 mL) per 12 week period to achieve the desired P loading. Nutrient analysis of the P source materials applied to the soil columns is provided in Table 2.

### **Subsoil saturation**

We tried to mimic two types of field drainage conditions with intact soil columns. We represented the controlled drainage by saturating subsoils, while we did not saturate subsoils for the uncontrolled drainage treatment (free-draining system). To monitor the water table, a hole (0.64-cm diameter) was drilled in the side of each column (10 cm from bottom of the column) and a Tygon tube was connected to the side of the column (Figure 1). A constant head apparatus was used to saturate and maintain the water level in the column at targeted height (50-cm from bottom of column). During saturation, we encountered a problem that water table could not be established in the soil columns from Cape Fear, Goldsboro and Wasda apparently due to the presence of highly restrictive layers in their subsoils. As a result, we could saturate subsoil in the columns from the Autryville soil only. Leachate samples from subsoil saturated columns were directly collected from the Tygon tube connected at the side of column (Figure 1).



### **Soil and leachate analysis**

For each sampling site, an extra soil column was collected to a depth of 90 cm. These columns were dissected into 15-cm increments for soil analysis. All soil samples were air-dried, ground and passed through a 2-mm sieve. Soil samples were extracted for Mehlich-3 extractable P ( $P_{M3}$ ) (Mehlich, 1984) and oxalate extractable P, Al and Fe ( $P_{ox}$ ,  $Al_{ox}$  and  $Fe_{ox}$ ) at pH of 3 in the dark (Schoumans, 2000). The degree of P saturation was calculated as:

$$DPS_{ox} = [P_{ox} / 0.5 (Al_{ox} + Fe_{ox})] \times 100 \% \quad [1]$$

where  $P_{ox}$ ,  $Al_{ox}$  and  $Fe_{ox}$  are oxalate extractable  $P_{ox}$ ,  $Al_{ox}$  and  $Fe_{ox}$  elements in  $mmol\ kg^{-1}$  soil. Particle size analysis by hydrometer method was used to determine soil textures with clay content (Gee and Bauder, 1986). Soil pH was measured in a 1:1 water to soil ratio with a glass electrode and soil organic matter (OM) was determined by loss-on-ignition (Nelson and Sommers, 1996). We determined a saturated liquid capacity (LC) of a soil column (LC,  $cm^{-3}$ ) by:

$$LC = [1 - (\text{bulk density} / \text{particle density})] \times \text{soil volume} \quad [2]$$

The cumulative volume (CV) of column leachates was normalized as the number of column pore volumes (PV, dimensionless) leached as follows:

$$PV = CV / LC \quad [3]$$

The leachate P data were normalized as a volume-weighted DRP calculated as [(Mass

DRP leached, mg) / (Leachate volume leached, L)].

Leachate samples were collected at the time of water addition and stored at <4 °C until analysis. Leachate samples were filtered through a 0.45-µm membrane and analyzed for dissolved reactive P (DRP) and nitrate (NO<sub>3</sub>-N) using the Lachat QuickChem 8000 (Milwaukee, WI).

### **Statistical analysis**

For the statistical design, two-way factorial arrangements (4 soils and 3 P sources) on a completely randomized design with 4 replications were used, having the sampling site as an experimental unit. Analysis of variance (ANOVA) using the General Linear Model (GLM) procedure and Duncan's multiple range test were performed to test the effects of soil, P source applied and subsoil saturation on leachate volume and volume-weighted concentrations of DRP and NO<sub>3</sub>-N (SAS Institute, 2001).

## **RESULTS AND DISCUSSION**

### **Leachate volume drained**

The PV leached were significantly influenced by soil type and P source applied (Figure 2). When averaged by soil type, Duncan's multiple range test ( $p < 0.10$ ) showed

that the PV leached was in the order of Autryville ( $2.98 \pm 0.08$ ) > Goldsboro ( $2.18 \pm 0.04$ ), Wasda ( $1.96 \pm 0.02$ ), and Cape Fear ( $1.24 \pm 0.05$ ). We observed that Autryville and Goldsboro soils were well drained while Cape Fear and Wasda soils were poorly drained in the course of the experiment, which are consistent with the description for these soils in Table 1. The P source types applied also affected the PV leached (Figure 2). The Autryville and Goldsboro columns treated with SL produced higher PV than those with PL and TSP due to extra-water added through SL irrigation (approximately 1.1 PV). The addition of SL to the Cape Fear and Wasda columns, however, did not result in increased PV because the applied SL appear to pond at the column surface during the experiment. We observed a very slow infiltration on the top soils, which is likely to be attributable the physical blocking of pores caused by organic particles in SL (Rowse et al., 1985).

### **Volume-weighted dissolved reactive phosphorus in column leachate**

Since there were differences in the PV of leached water among soil columns, we present leachate P data based on the volume-weighted DRP. The volume-weighted DRP concentrations in the column leachates ranged from 0.01 to 0.035 mg P L<sup>-1</sup> (Table 3). Regardless of P source treatments, the DRP in Wasda soil (0.032 – 0.035 mg P L<sup>-1</sup>) was about three-fold greater than the other soils (0.01 – 0.018 mg P L<sup>-1</sup>). The DRP concentrations and the mass loss of DRP were significantly influenced by the soil type

but the influence of P source type was not significant ( $p < 0.01$ ). Assuming a piston-flow type of solute displacement, low pore volume leached (1.1 – 4.9 PV) from the study columns was likely to be insufficient for the surface-applied P to breakthrough to the bottom of a column. For example, the total mass of DRP leached ( $< 0.4 \text{ kg ha}^{-1}$ ) represented  $< 0.1 \%$  of the applied P ( $400 \text{ kg total P ha}^{-1}$ ) (Table 3). Moreover, we observed that 4 to 11 PV of water was needed for peak discharge of P from top 10-cm Autryville soils (Chapter 2). Taking into account this result, it was reasonable to think that most applied P was retained in topsoils (0-15 cm) and the DRP in column leachates mostly came from desorbed P from the subsoils (75-90 cm).

### **Leachate phosphorus concentration in relation to soil test P**

In NC, researchers recognize a critical agronomic  $P_{M3}$  level of  $53 \text{ mg kg}^{-1}$  in surface soils (0-20 cm) (Johnson, 2004). The  $P_{M3}$  in surface soils (0-15 cm) of the study columns ranged from 51 to  $349 \text{ mg kg}^{-1}$  with a median of  $185 \text{ mg kg}^{-1}$  (Table 4), indicating an excessive P fertilization at the sampling sites. The volume-weighted DRP concentration in column leachates did not show any relationship with the  $P_{M3}$  in surface soils (0-15 cm), given the limited leachate volume achieved (Figure 3).

North Carolina's phosphorus loss assessment tool (PLAT) assesses P leaching potential by two algorithms distinctly targeting soil textural groups in surface soils. For

example, if the  $P_{M3}$  in surface soils exceeds the threshold levels (50, 100, 200 and 500 mg  $kg^{-1}$  for “organic”, “sands”, “loams” and “clay” , respectively), subsoil sampling at a depth of 76.2 cm is required to estimate leachate P concentration (NC PLAT Committee, 2005). If the  $P_{M3}$  in surface soils is equal or less than the threshold  $P_{M3}$  concentrations, the leachate P concentration at the 76.2 cm depth is assumed to be 0.0 mg  $L^{-1}$ . Based on these guidelines, half of our sampling sites had a risk of P leaching potential and subsoil sampling would be required to measure the  $P_{M3}$  at a depth 76 cm.

Figure 4 shows the relationship between the  $P_{M3}$  of subsoils (75-90 cm) and volume-weighted DRP in leachates. The DRP concentration in the leachates collected at deep subsoil (>90 cm) was <0.02 mg  $L^{-1}$ , except those from Wasda soils (0.032 to 0.035 mg  $L^{-1}$ ).. The higher DRP concentration in Wasda soils treated with swine liquid (SL) and poultry litter (PL) compared to other soils may be attributable to higher Mehlich-3 P present in deep subsoils (22 and 69 mg  $kg^{-1}$  at 75-90 cm depth) than the other soils (0-7 mg  $kg^{-1}$  at 75-90 cm depth). The reason why there was an increase of DRP in Wasda columns treated with TSP (0.032 mg  $L^{-1}$ ), which had no extractable P ( $P_{M3}$ ) present in their subsoils (0 mg  $kg^{-1}$ ) is not clear from our data.

### **Degree of phosphorus saturation through soil profile**

Hooda et al. (2000) noted that an agronomic test alone may overestimate the P fraction that might be released to percolating waters. Rather, they suggested the use of degree of P saturation, which incorporates both soil P concentration and P sorption capacity of a soil when examining whether the soil might leach P. A  $DPS_{ox}$  of 25 % has often been referred to as the threshold that may cause rapidly elevated P in soil solution (Maguire and Sims, 2002; Nair et al., 2004; Butler and Coale, 2005). Figure 5 shows initial  $DPS_{ox}$  in soil columns prior to P source addition with depth segmented by soil and previous P source history. A consistent pattern was that the  $DPS_{ox}$  in most surface soils were greater than 25 %, but it decreased with depth to well below 25% of  $DPS_{ox}$  with increasing depth.

This result suggests that vertical P movement in our study columns would be further limited by the P sorption capacity of subsoils especially below the root zone (>50 cm), even if larger quantities of water were leached. One exception was Wasda organic muck, which had a  $DPS_{ox}$  of <25 % in surface soils but P appeared to move down to deep subsoils with less P retention than other soils. This result suggests that downward movement of P in organic-rich soils could be preceded without saturating the upper soils in terms of P, highlighting enhanced P mobility in organic-rich soils. The enhanced P mobility in Wasda soils is in agreement with the result of Chapter 1 in that the ability of

non-crystalline oxides of Al and Fe in sorbing P decreased in mineral-organic soils compared in mineral soils (Chapter 1, Figure 9), emphasizing the unique P sorption mechanism in organic-rich soils.

### **Factors attributable to the low phosphorus concentration in column leachates**

Low P concentrations (0.01 to 0.035 mg DRP L<sup>-1</sup>) in our column leachates emphasize the importance of subsoil properties for P leaching. The typically lower pH of the subsoils would tend to increase their P sorption capacity (Table 4). The ability of subsoil to retain P, which can be approximated by (Al<sub>ox</sub> + Fe<sub>ox</sub>), may be more important for P leaching than extractable P concentration in the topsoil (Djordjic et al., 2004). The Autryville, Goldsboro and Cape Fear soils had greater concentrations of (Al<sub>ox</sub> + Fe<sub>ox</sub>) in subsoils compared with surface soils (Figure 6), suggesting a greater P sorption capacity of these subsoils compared with the surface soils. Exception was the Wasda soils which showed a decrease in (Al<sub>ox</sub> + Fe<sub>ox</sub>) with increasing depth. Accordingly, the Wasda subsoils had lower P sorption capacity compared with the surface soils and this would be the reason why we observed higher P<sub>M3</sub> concentration in Wasda soils than the other soils.

Extractable P (P<sub>M3</sub> or P<sub>ox</sub>) at start of experiment was lower in subsoils than in surface soils (Figure 7), and accordingly, the DPS<sub>ox</sub> was lower in subsoils than in surface soils. Therefore, P transport would be slower in the subsoil than in the corresponding surface

soil for a given amount water leached (1.1 – 4.9 PV). It typically took 4 to 11 column PV of water for surface-applied P to have a peak discharge in the top 10-cm of surface soil (Chapter 2, Figure 8). Accordingly, it would take 36 and 99 column PV of water for surface-applied P to be displaced in the 90-cm long columns. Given amount of water leached in the 90-cm long column (1.1 – 4.9 PV) was clearly insufficient to observe a peak discharge of surface-applied P source materials. The fact that we observed only a maximum of 0.09 % of applied P in column leachates (Table 3) is probably more a factor of the lack of water throughput than any other soil properties.

### **Effects of subsoil saturation on the loss of nitrate and phosphorus**

We monitored the concentrations of NO<sub>3</sub>-N and DRP concentrations from subsoil-saturated columns for a 36 week period as compared to the unsaturated columns. There was no significant difference in the PV of leached water between subsoil saturation treatments ( $p < 0.05$ ). We found that the subsoil saturation affected the concentration of NO<sub>3</sub>-N significantly, while it did not affect the concentration of DRP ( $p < 0.05$ ). The decreased concentration of NO<sub>3</sub>-N under saturated subsoils compared to unsaturated subsoils was consistent among the types of P source materials applied, showing a decrease in the concentration of NO<sub>3</sub>-N by 35 to 44 % (Figure 8). However, the differences of DRP concentration between saturated and unsaturated subsoils were not



significant, and the DRP concentration remained below  $0.02 \text{ mg L}^{-1}$  regardless of P source materials applied (Figure 9). It should be noted that the leachate samples in the subsoil-saturated columns were not taken anoxically, and in fact some leachate samples showed a sign of Fe-oxide precipitation as a red-colored precipitate. The Fe-oxide precipitate would sorb any dissolved P after sampling and remove it during filtration, underestimating real dissolved P in the leachate samples.

## CONCLUSIONS

For 90-cm long columns representing four soil types leached with a limited volume of water (PV leached =  $2.1 \pm 0.1$  after applying  $400 \text{ kg total P ha}^{-1}$ ), the volume-weighted DRP concentration in most column leachates was below  $0.4 \text{ mg L}^{-1}$ . Assuming a piston-type of P displacement, surface-applied P was most likely to be retained for the given PV of leached water. We found no relationship between  $P_{M3}$  in surface soils and DRP concentration in leachates. Moreover,  $DPS_{ox}$  through soil profile at start of experiment indicated that most subsoils had sufficient P sorption capacity to retain any soluble P, even if a larger PV was leached.

Nonetheless the organic-rich soil (Wasda muck) in our study showed a potential of deep leaching of P. The  $DPS_{ox}$  in Wasda surface soils (16-21 % at 0-15 cm) were

below a  $DPS_{ox}$  threshold (25 %) but we observed significant  $DPS_{ox}$  in deep subsoils (9-14 % at 75-90 cm), implying that downward movement of P in organic-rich soils could be preceded without the P saturation of upper soils especially when receiving organic P source materials (e.g., poultry litter and swine liquid). The significantly higher DRP concentration in Wasda soil columns (0.032 – 0.035 mg L<sup>-1</sup>) than other mineral soils (<0.02 mg L<sup>-1</sup>) suggests that the deep leaching of P may occur in organic-rich soils. In addition, current recommendations of subsoil sampling in NC PLAT to assess a deep P leaching potential (50, 100, 200 and 500 mg P<sub>M3</sub> kg<sup>-1</sup> for organic”, “sands”, “loams” and “clay”, respectively) were found to be conservative to minimize P leaching losses based on our data from limited water throughput.

The lack of number of pore volume leached in our study permitted speculation on the incomplete P displacement with a matrix flow in a column scale. Considering a high affinity of P to the soil, water irrigation that could be sufficient for the applied P or higher surface soil P to breakthrough will be essential in studying vertical P transport. Preferential flow conditions (e.g., natural channels, fissures and structural voids) have an important role in predicting vertical P transport since they will allow dissolved P to bypass the soil matrix with little adsorption to the soil. Our study did not cover the role of preferential flow on the P leaching and detailed investigation on this topic is required to fully understand environmental consequences of P leaching.

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**Table 1. Soil management groups (SMG) of study soils (Hodges, 2001).**

Soil series	SMG†	Description
Autryville	27	Well to excessively drained mineral soils; Loamy particle size class with Bt 20 to 40 inches (Arenic).
Cape Fear	6	Mineral-organic soils of the Coastal Plains: Histic < 16 inches or umbric epipedons. Very poorly drained. Fine and silty particle size class
Goldsboro	20	Moderately well drained mineral soils: Fine loamy and coarse loamy particle size class.
Wasda	7	Mineral-organic soils of the Coastal Plains: Histic <16 inches or Umbric epipedons. Very poorly drained. Loamy particle size classes.

† Soil management group

**Table 2. Nutrient analysis of triplesuperphosphate, poultry litter, and swine effluent.**

P source materials	Total N	Total P	Total C	Dry matter
		g kg <sup>-1</sup>		%
Poultry litter	29	29	189	71
Swine liquid	1	0	N.A.†	0.3
Triplesuperphosphate	0	198	0	100

† Not available.

**Table 3. Pore volume leached, volume-weighted DRP and mass of DRP leached over the 48 weeks of leaching period.**

Soil	P source applied <sup>†</sup>	Pore volume leached	Volume-weighted DRP	Mass of DRP leached	DRP leached from applied materials <sup>§</sup>
			mg L <sup>-1</sup>	kg ha <sup>-1</sup>	%
Autryville	Poultry litter	2.16 (0.01) <sup>‡</sup>	0.010 (0.000)	0.12 (0.00)	0.03
	Swine liquid	4.29 (0.09)	0.010 (0.000)	0.16 (0.01)	0.04
	TSP	2.81 (0.01)	0.018 (0.002)	0.19 (0.02)	0.05
Cape Fear	Poultry litter	1.53 (0.02)	0.015 (0.001)	0.13 (0.02)	0.03
	Swine liquid	1.10 (0.01)	0.013 (0.002)	0.08 (0.01)	0.02
	TSP	1.01 (0.04)	0.017 (0.002)	0.08 (0.01)	0.02
Goldsboro	Poultry litter	1.88 (0.08)	0.013 (0.001)	0.12 (0.01)	0.03
	Swine liquid	2.55 (0.04)	0.013 (0.001)	0.17 (0.01)	0.04
	TSP	1.92 (0.02)	0.015 (0.004)	0.14 (0.03)	0.04
Wasda	Poultry litter	2.25 (0.03)	0.035 (0.002)	0.36 (0.02)	0.09
	Swine liquid	1.65 (0.06)	0.033 (0.006)	0.23 (0.04)	0.06
	TSP	1.92 (0.01)	0.032 (0.004)	0.28 (0.04)	0.07

<sup>†</sup> The amount of P source materials applied for the 48 weeks of leaching period was 400 kg ha<sup>-1</sup>.

<sup>‡</sup> Values in parentheses are a standard error of the mean.

<sup>§</sup> Calculated by  $100 \times [(\text{Mass of DRP leached}) / (\text{the amount of P source materials applied})]$ .

**Table 4. Selected soil properties by depth at start of experiment.**

Soil	P source history	Depth cm	pH	Clay	Organic matter	P <sub>M3</sub> †	P <sub>ox</sub> ‡	Al <sub>ox</sub> +Fe <sub>ox</sub> §	DPS <sub>ox</sub> ¶
				g kg <sup>-1</sup>	g kg <sup>-1</sup>	mg kg <sup>-1</sup>	mg kg <sup>-1</sup>	mmol kg <sup>-1</sup>	%
Autryville	TSP	0-15	6.4	11	9	204	192	16	77
		15-30	6.0	21	5	95	100	12	55
		30-45	5.3	31	5	27	29	8	24
		45-60	5.1	23	4	15	20	7	18
		60-75	4.9	44	8	6	9	9	6
	Poultry litter	75-90	4.8	44	7	5	8	9	6
		0-15	5.3	17	13	205	220	15	95
		15-30	4.9	25	8	174	172	14	77
		30-45	4.7	41	8	98	108	12	60
		45-60	4.5	143	44	39	80	40	13
	Swine liquid	60-75	4.5	146	40	1	12	38	2
		75-90	4.8	151	38	2	14	34	3
		0-15	6.4	13	13	202	172	13	86
		15-30	7.0	9	6	150	160	12	83
		30-45	6.9	27	3	40	40	6	46
Cape Fear	TSP	45-60	4.5	75	17	6	14	21	4
		60-75	4.7	229	55	5	12	90	1
		75-90	4.6	194	52	4	10	92	1
		0-15	5.8	15	57	118	232	98	15
		15-30	5.4	23	48	56	112	82	9
	Poultry litter	30-45	4.6	198	46	3	12	117	1
		45-60	4.7	242	57	4	13	106	1
		60-75	4.7	229	55	5	12	90	1
		75-90	4.6	194	52	4	10	92	1
		0-15	6.1	16	51	120	212	54	25
	Swine liquid	15-30	5.8	15	46	78	144	61	15
		30-45	4.8	16	32	7	17	58	2
		45-60	4.7	22	39	5	12	63	1
		60-75	4.7	165	39	5	12	52	1
		75-90	4.7	160	35	4	9	48	1
Goldsboro	TSP	0-15	5.9	18	101	275	600	77	50
		15-30	5.8	21	76	104	204	81	16
		30-45	5.1	14	52	51	112	114	6
		45-60	4.9	186	51	23	48	95	3
		60-75	4.9	188	47	23	40	84	3
	Poultry litter	75-90	4.8	194	47	8	26	108	2
		0-15	5.0	44	14	295	364	20	115
		15-30	5.4	157	14	404	440	26	108
		30-45	4.9	187	31	143	192	33	37
		45-60	4.5	204	30	10	24	26	6
	Swine liquid	60-75	4.5	255	30	1	4	19	1
		75-90	4.4	239	29	4	6	17	2
		0-15	6.1	17	20	349	440	26	111
		15-30	5.7	32	29	161	216	28	49
		30-45	4.7	114	38	21	35	36	6
Wasda	TSP	45-60	4.5	114	40	4	11	37	2
		60-75	4.4	139	49	1	4	42	1
		75-90	4.4	130	46	2	8	43	1
		0-15	5.2	30	26	51	120	44	18
		15-30	4.7	105	20	5	14	33	3
	Poultry litter	30-45	4.5	100	19	2	6	24	2
		45-60	4.5	101	22	1	5	30	1
		60-75	4.5	101	19	1	5	28	1
		75-90	4.5	127	26	0	3	26	1
		0-15	4.4	9	451	146	440	169	17
	Swine liquid	15-30	4.2	17	289	196	680	272	16
		30-45	4.2	12	95	55	160	101	10
		45-60	4.3	7	39	21	38	48	5
		60-75	4.4	66	23	2	8	21	2
		75-90	4.4	69	35	0	4	20	1
Wasda	TSP	0-15	5.0	12	244	131	520	161	21
		15-30	4.8	14	233	103	480	152	20
		30-45	5.1	11	242	104	380	177	14
		45-60	5.2	18	179	77	336	158	14
		60-75	5.1	16	157	69	292	145	13
	Poultry litter	75-90	4.9	11	55	69	160	75	14
		0-15	4.8	10	266	119	396	158	16
		15-30	4.8	10	99	36	104	112	6
		30-45	4.8	12	28	11	18	45	3
		45-60	4.8	130	31	2	7	36	1
	Swine liquid	60-75	5.0	122	28	4	8	38	1
		75-90	5.2	63	25	22	30	20	9

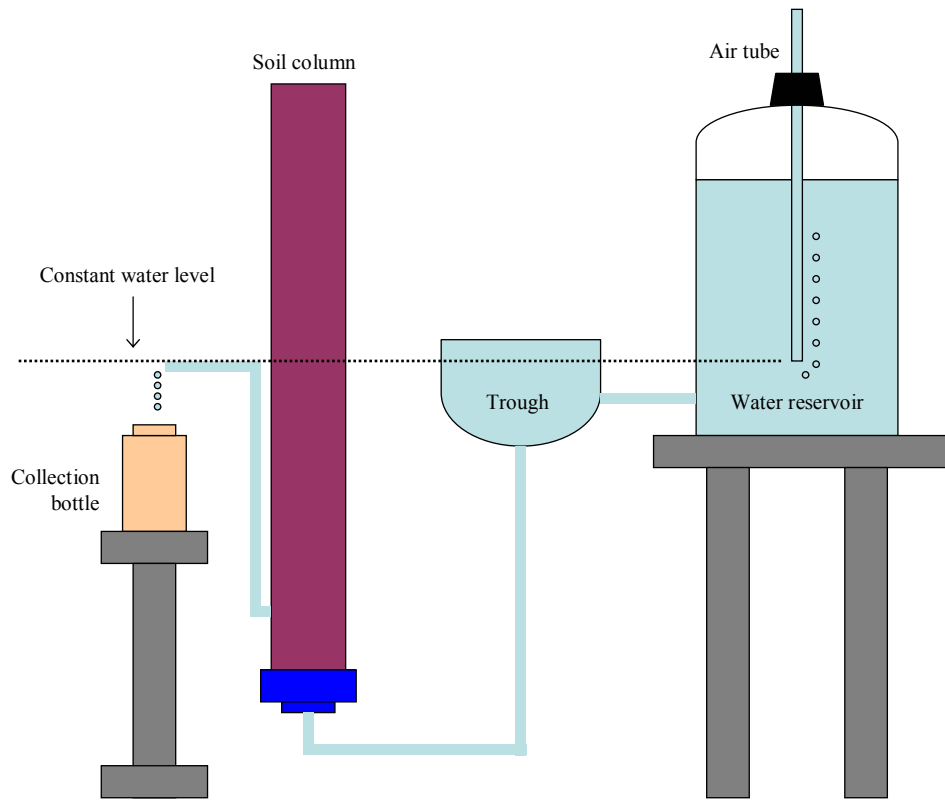
† Mehlich-3 extractable P.

‡ Ammonium-oxalate extractable P, Al, and Fe, respectively.

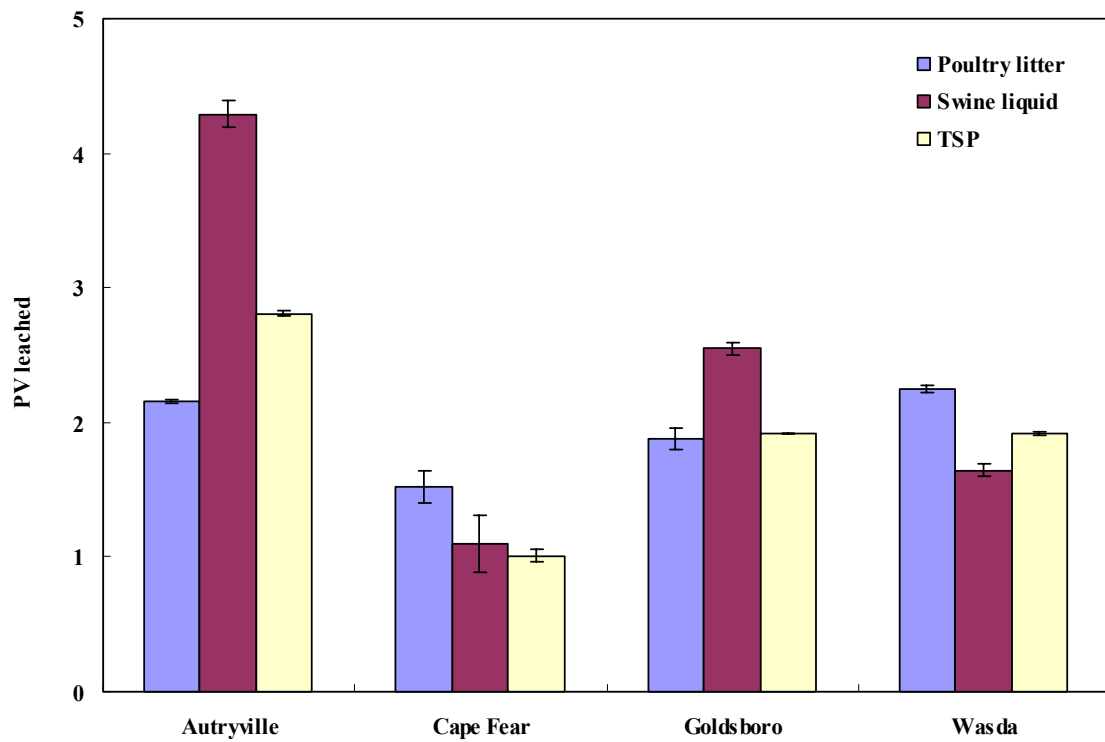
§ Sum of oxalate extractable Al and Fe.

¶ Degree of P saturation calculated as the molar ratio of  $100 \times P_{ox} / (0.5 \times [Al_{ox} + Fe_{ox}])$ .

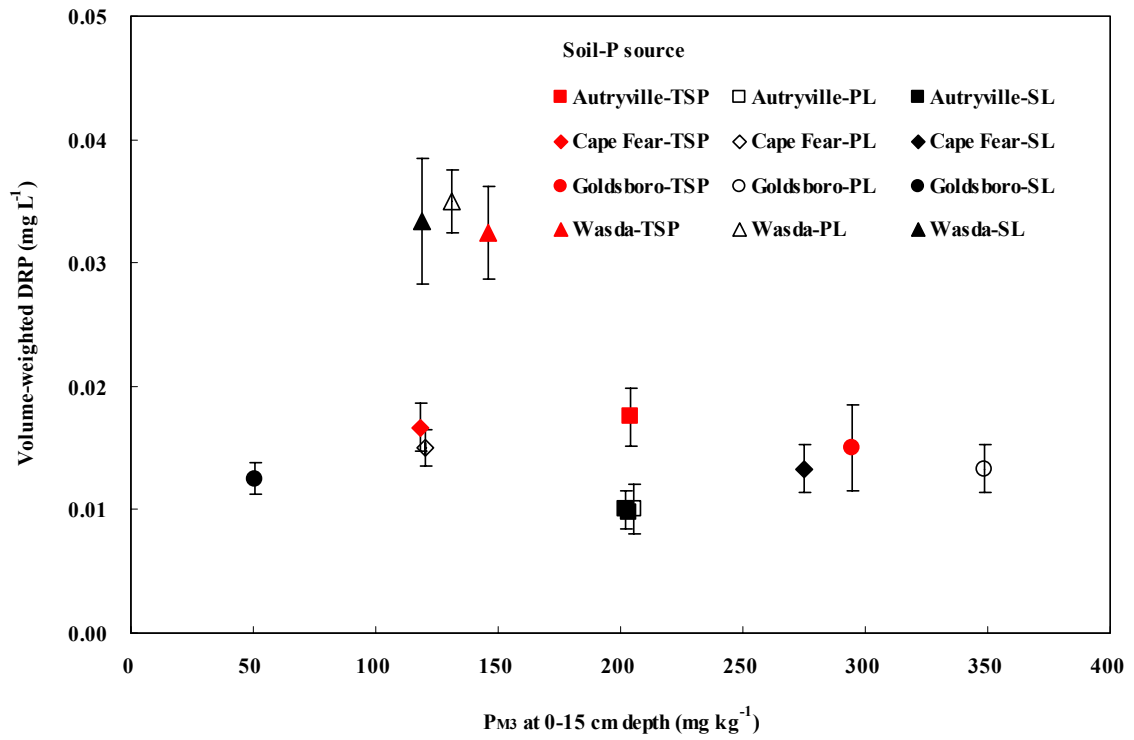




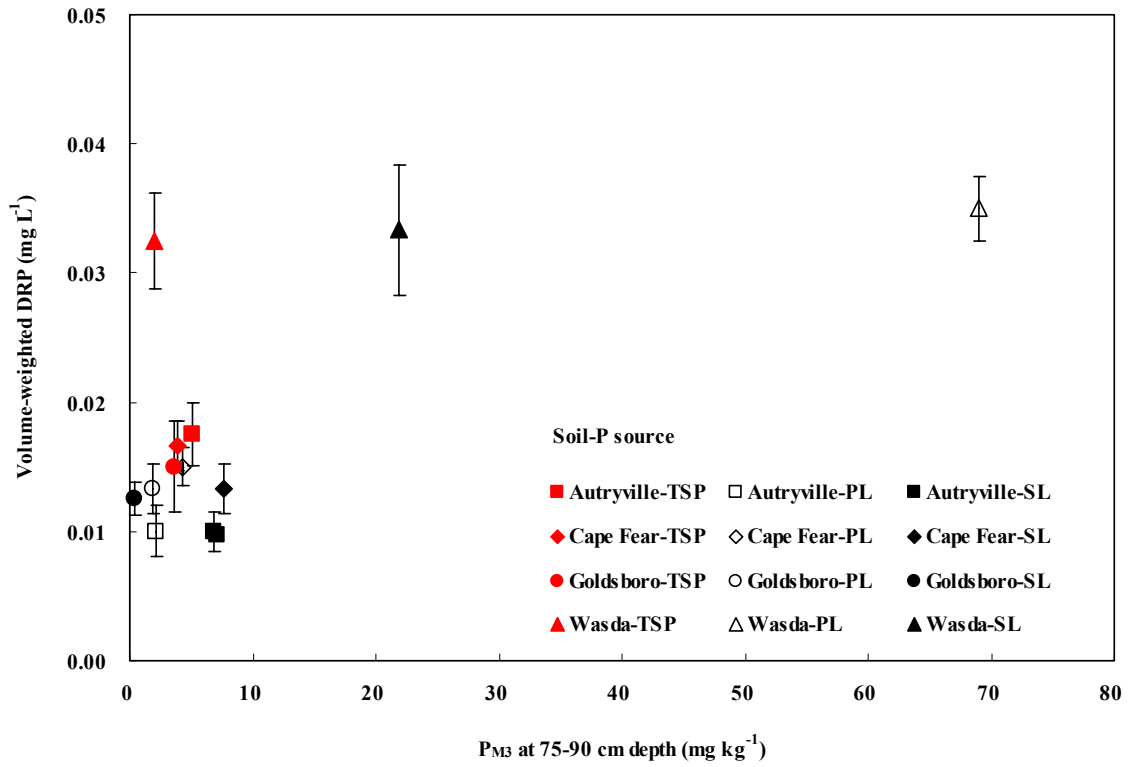
**Figure 1. Schematic diagram of a constant-head apparatus used to establish water table.**



**Figure 2. The number of pore volume leached in soil  $\times$  P source treatments.**



**Figure 3. Relationship between the volume-weighted DRP and the Mehlich-3 P ( $P_{M3}$ ) of surface soils (0-15 cm). Error bars indicates standard error of the mean volume-weighted DRP.**



**Figure 4. Relationship between the volume-weighted dissolved DRP and the Mehlich-3 P ( $P_{M3}$ ) of subsoils (75-90 cm). Error bars indicate standard error of the mean volume-weighted DRP.**

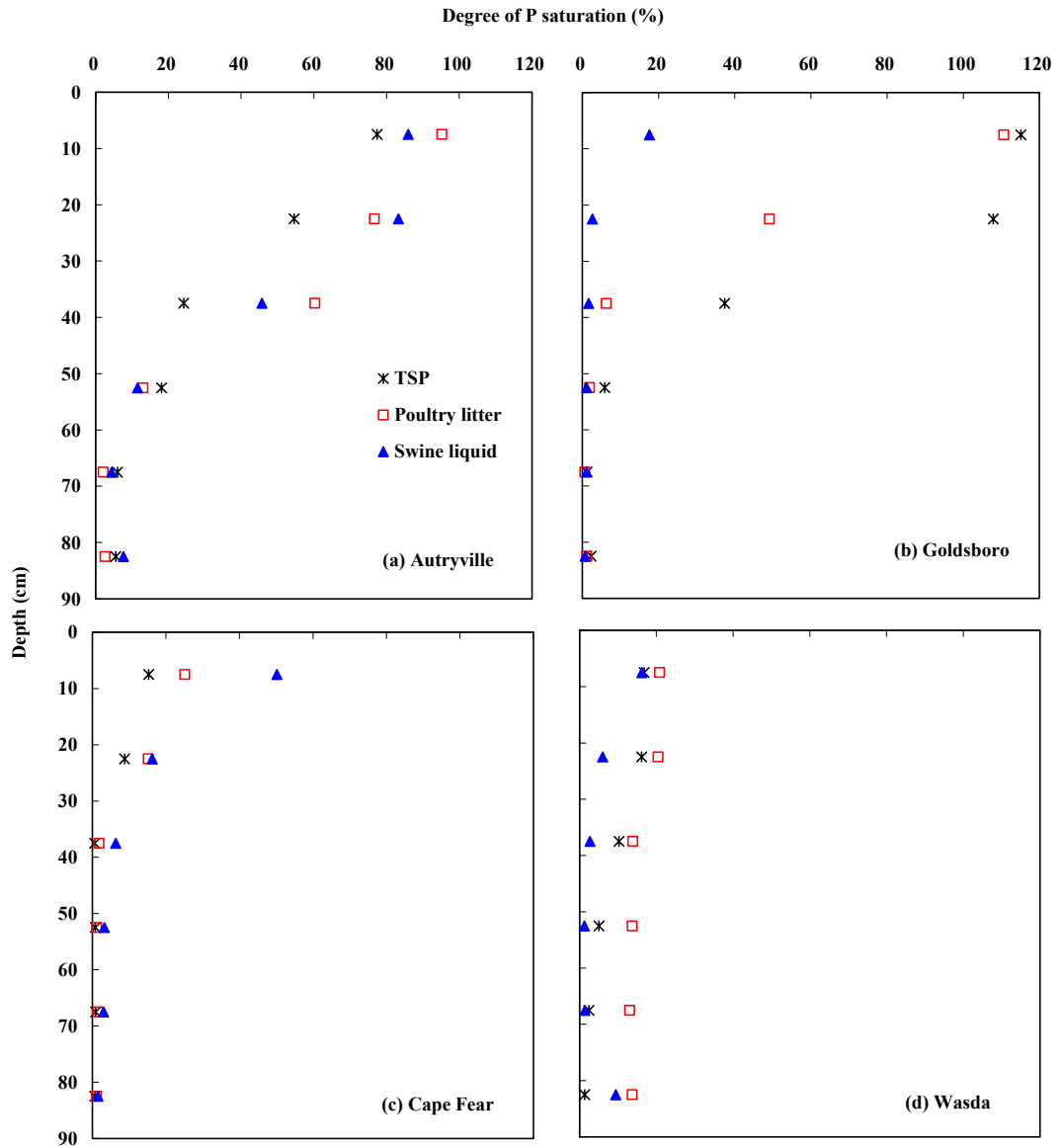
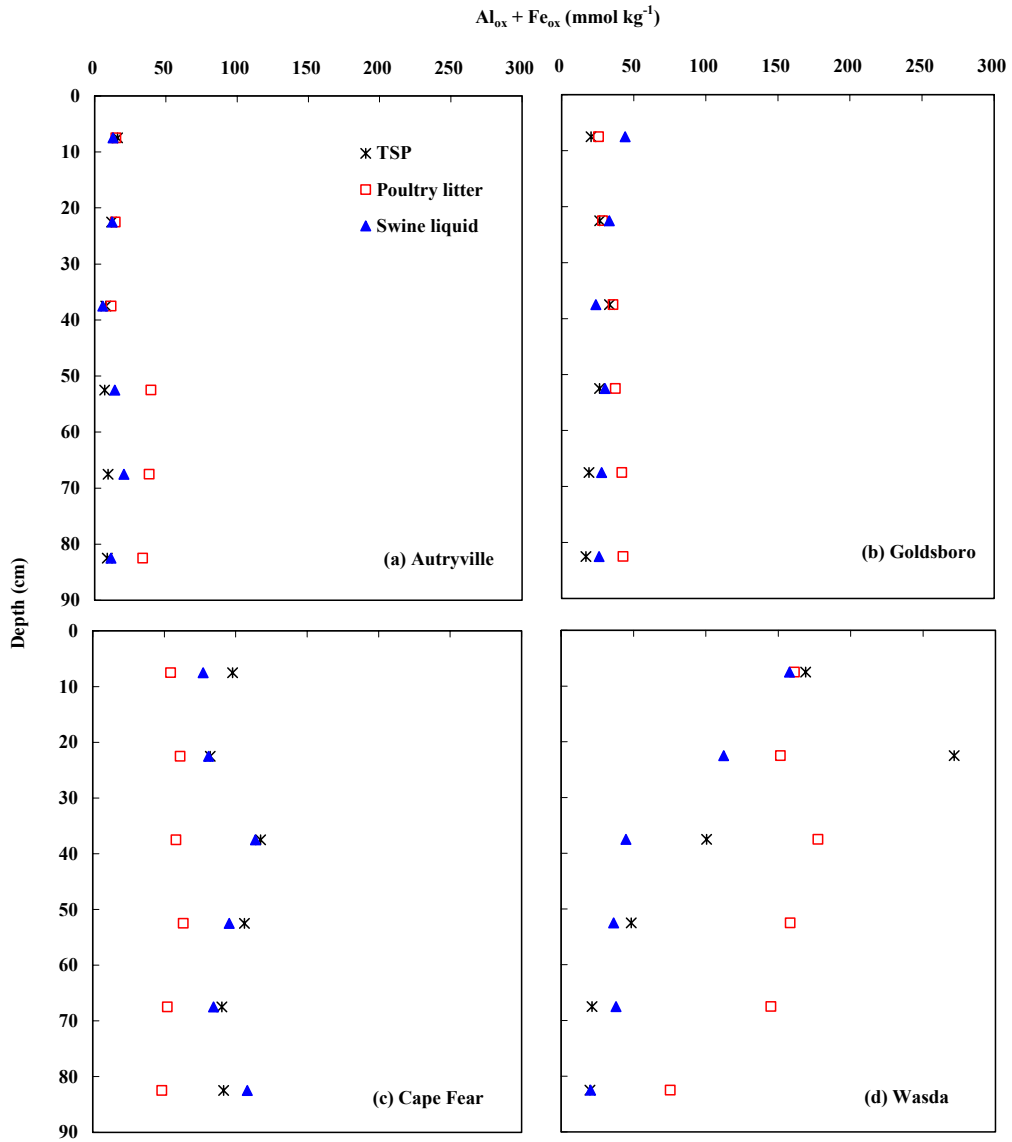


Figure 5. Degree of P saturation ( $DPS_{ox}$ ) with depth in (a) Autryville, (b) Goldsboro, (c) Cape Fear and (d) Wasda soils prior to P source application.



**Figure 6. Sum of oxalate-extractable Al and Fe with depth in (a) Autryville, (b) Goldsboro, (c) Cape Fear, and (d) Wasda soils.**

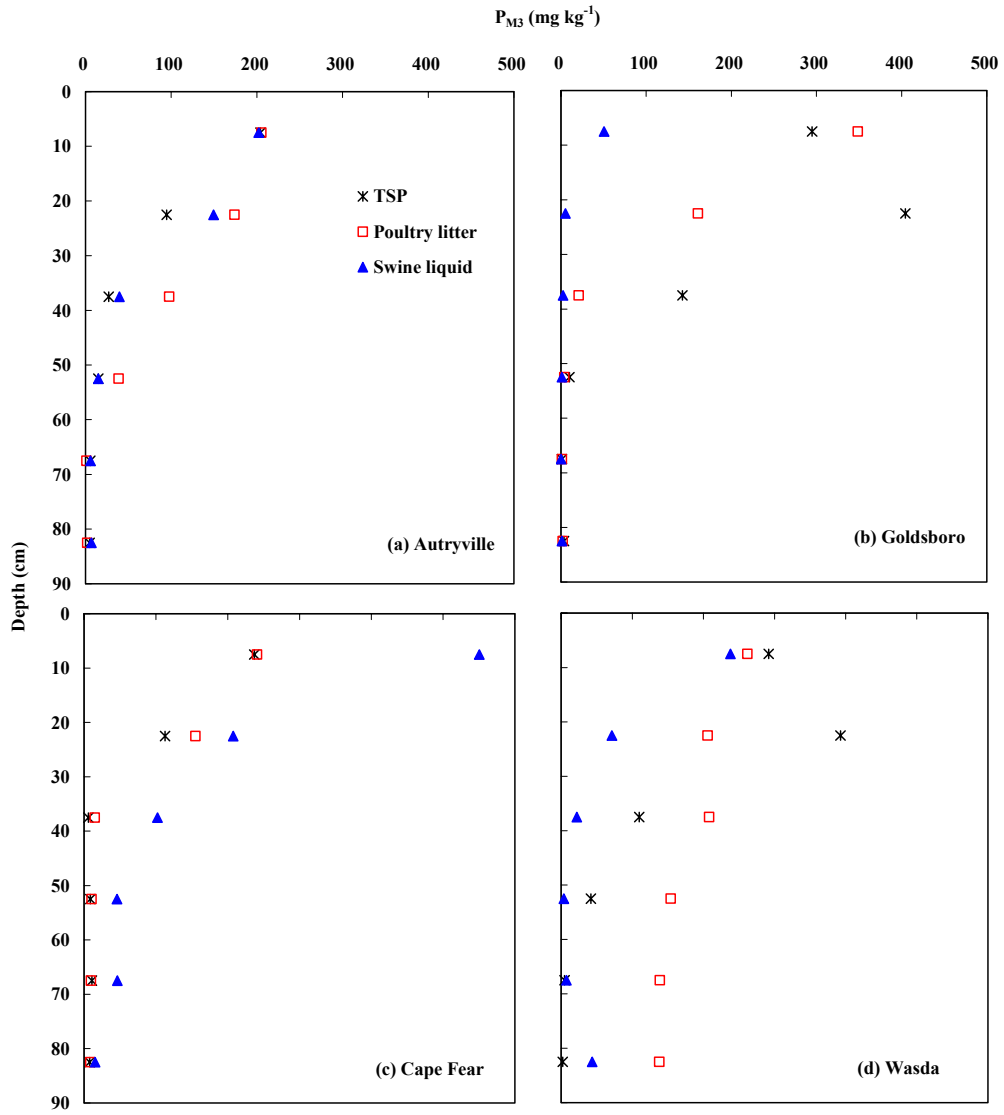
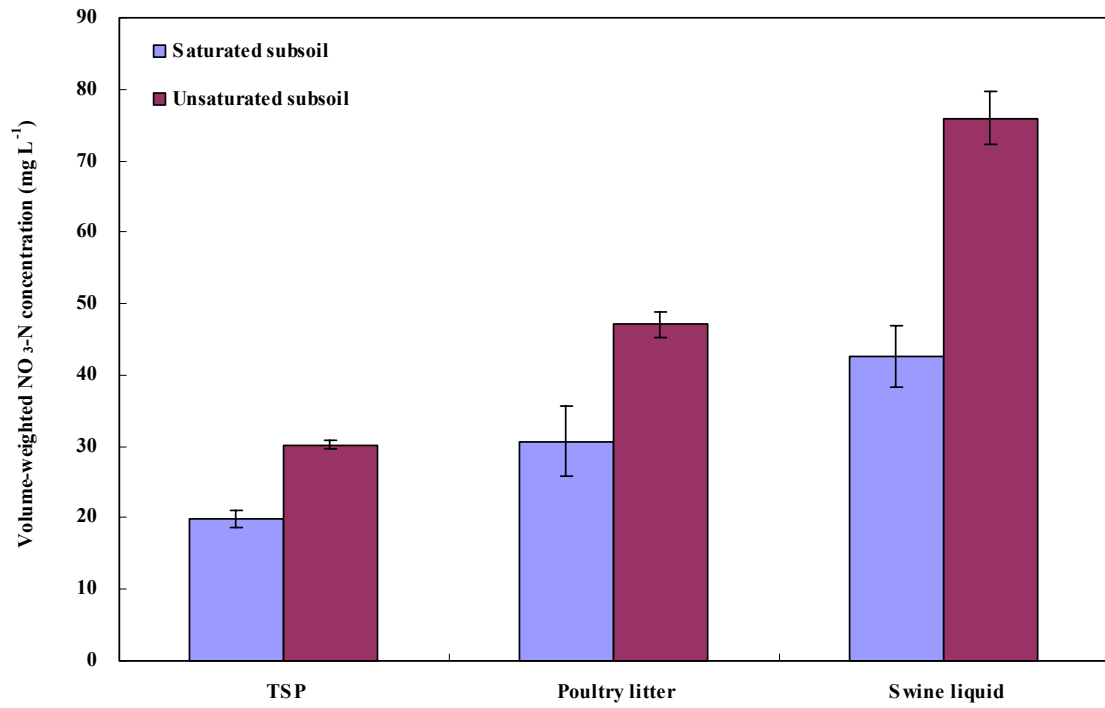
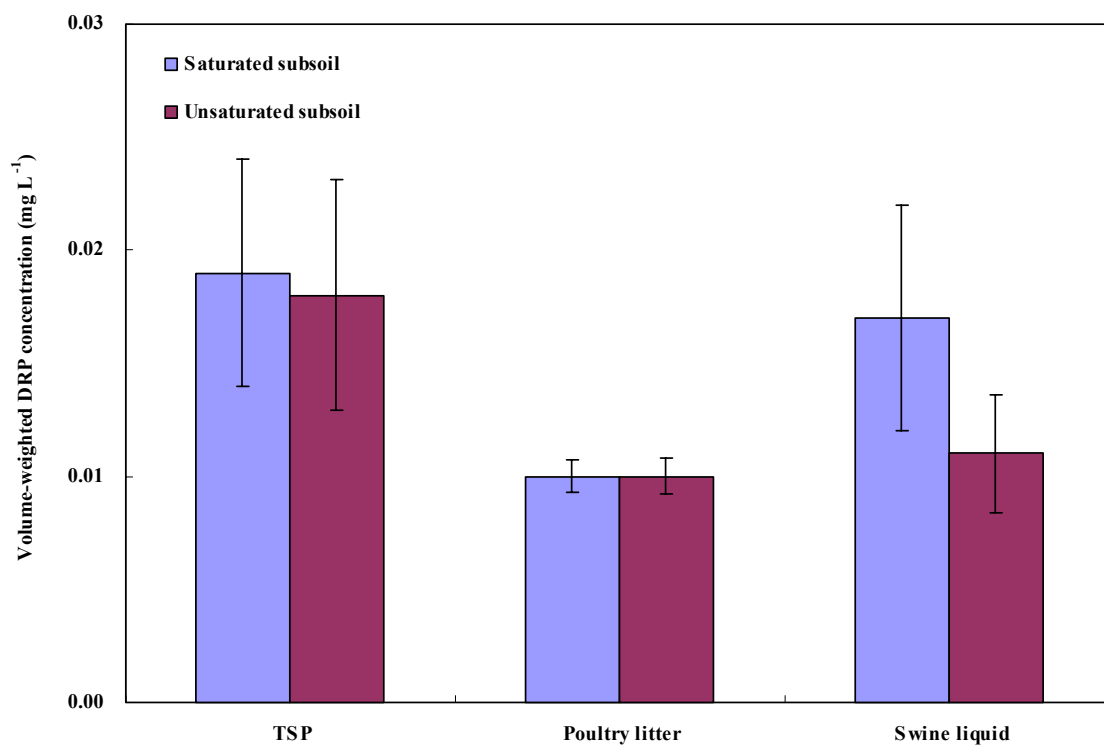


Figure 7. Mehlich-3 P ( $P_{M3}$ ) with depth in (a) Autryville, (b) Goldsboro, (c) Cape Fear, and (d) Wasda soils.



**Figure 8. Comparison of nitrate (NO<sub>3</sub>-N) concentration between saturated and unsaturated subsoils in the Autryville soil.**





**Figure 9. Comparison DRP concentration between saturated and unsaturated subsoils in the Autryville soil.**

## Appendix A. Supporting materials for chapter 1

**Table 1. The SAS output for stepwise regression of soil properties against  $S_{max}$  in the oxalate model as a single variable of  $[Al + Fe]$ .**

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**Oxalate model: as a single variable of  $[Al_{ox} + Fe_{ox}]$**

---

Dependent Variable: Smax

Stepwise Selection: Step 1

Variable AlFeox Entered: R-Square = 0.6104 and C(p) = 157.9715

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	9469.97167	9469.97167	109.68	<.0001
Error	70	6043.90333	86.34148		
Corrected Total	71	15514			

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	9.04362	1.64326	2615.10597	30.29	<.0001
AlFeox	0.21908	0.02092	9469.97167	109.68	<.0001

Bounds on condition number: 1, 1

Stepwise Selection: Step 2

Variable Clay Entered: R-Square = 0.8624 and C(p) = 13.7878

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	13380	6689.92324	216.31	<.0001
Error	69	2134.02851	30.92795		
Corrected Total	71	15514			

The REG Procedure

Model: MODEL1

Dependent Variable: Smax

Stepwise Selection: Step 2

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	0.88463	1.22223	16.20208	0.52	0.4716
Clay	0.05937	0.00528	3909.87482	126.42	<.0001
AlFeox	0.22603	0.01254	10056	325.13	<.0001

---

**Table 1 (continued).**

---

**Oxalate model: as a single variable of [Al<sub>ox</sub> + Fe<sub>ox</sub>]**

---

Stepwise Selection: Step 3

Variable pH Entered: R-Square = 0.8841 and C(p) = 3.2292

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	13716	4571.91389	172.90	<.0001
Error	68	1798.13334	26.44314		
Corrected Total	71	15514			

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	22.72524	6.23135	351.69467	13.30	0.0005
pH	-3.94812	1.10776	335.89517	12.70	0.0007
Clay	0.05011	0.00553	2169.32207	82.04	<.0001
AlFeox	0.21345	0.01212	8207.51175	310.38	<.0001

Bounds on condition number: 1.3611, 11.23

Stepwise Selection: Step 4

Variable pH Removed: R-Square = 0.8624 and C(p) = 13.7878

stepwise regression of oxalate model with (Al+Fe)ox

The REG Procedure

Model: MODEL1

Dependent Variable: Smax

Stepwise Selection: Step 4

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	13380	6689.92324	216.31	<.0001
Error	69	2134.02851	30.92795		
Corrected Total	71	15514			

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	0.88463	1.22223	16.20208	0.52	0.4716
Clay	0.05937	0.00528	3909.87482	126.42	<.0001
AlFeox	0.22603	0.01254	10056	325.13	<.0001

Bounds on condition number: 1.0024, 4.0097

---

**Table 1 (continued).**

---

**Oxalate model: as a single variable of [Al<sub>ox</sub> + Fe<sub>ox</sub>]**

---

All variables left in the model are significant at the 0.0001 level.

The stepwise method terminated because the next variable to be entered was just removed.

Summary of Stepwise Selection								
Step	Variable Entered	Variable Removed	Number Vars In	Partial R-Square	Model R-Square	C(p)	F Value	Pr > F
1	AlFeox		1	0.6104	0.6104	157.971	109.68	<.0001
2	Clay		2	0.2520	0.8624	13.7878	126.42	<.0001
3	pH		3	0.0217	0.8841	3.2292	12.70	0.0007
4		pH	2	0.0217	0.8624	13.7878	12.70	0.0007

The REG Procedure

Model: MODEL1

Dependent Variable: Smax

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	13380	6689.92324	216.31	<.0001
Error	69	2134.02851	30.92795		
Corrected Total	71	15514			
	Root MSE	5.56129	R-Square	0.8624	
	Dependent Mean	21.87500	Adj R-Sq	0.8585	
	Coeff Var	25.42304			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t	Standardized Estimate
Intercept	1	0.88463	1.22223	0.72	0.4716	0
Clay	1	0.05937	0.00528	11.24	<.0001	0.50263
AlFeox	1	0.22603	0.01254	18.03	<.0001	0.80607

---

**Table 2. The SAS output for stepwise regression of soil properties against  $S_{max}$  in the oxalate model as separate  $Al_{ox}$  and  $Fe_{ox}$ .**

---

**Oxalate model: as separate  $Al_{ox}$  and  $Fe_{ox}$**

---

Dependent Variable: Smax

Stepwise Selection: Step 1

Variable Alox Entered: R-Square = 0.5733 and C(p) = 196.7718

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	8893.59644	8893.59644	94.04	<.0001
Error	70	6620.27856	94.57541		
Corrected Total	71	15514			

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	10.40481	1.64701	3774.47134	39.91	<.0001
Alox	0.25217	0.02600	8893.59644	94.04	<.0001

Bounds on condition number: 1, 1

---

Stepwise Selection: Step 2

Variable Clay Entered: R-Square = 0.8824 and C(p) = 6.9649

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	13689	6844.74112	258.87	<.0001
Error	69	1824.39275	26.44047		
Corrected Total	71	15514			

The REG Procedure

Model: MODEL1

Dependent Variable: Smax

Stepwise Selection: Step 2

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	0.76987	1.12702	12.33783	0.47	0.4968
Clay	0.06614	0.00491	4795.88580	181.38	<.0001
Alox	0.27414	0.01385	10365	392.02	<.0001

Bounds on condition number: 1.0141, 4.0563

---

**Table 2 (continued).**

---

**Oxalate model: as separate Al<sub>ox</sub> and Fe<sub>ox</sub>**

---

Stepwise Selection: Step 3

Variable pH Entered: R-Square = 0.8923 and C(p) = 2.8056

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	13843	4614.49598	187.85	<.0001
Error	68	1670.38705	24.56452		
Corrected Total	71	15514			

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	15.93401	6.15290	164.73984	6.71	0.0117
pH	-2.72437	1.08806	154.00570	6.27	0.0147
Clay	0.05941	0.00544	2926.78812	119.15	<.0001
Alox	0.26188	0.01422	8335.25804	339.32	<.0001

Bounds on condition number: 1.4136, 11.715

Stepwise Selection: Step 4

Variable pH Removed: R-Square = 0.8824 and C(p) = 6.9649

The REG Procedure

Model: MODEL1

Dependent Variable: Smax

Stepwise Selection: Step 4

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	13689	6844.74112	258.87	<.0001
Error	69	1824.39275	26.44047		
Corrected Total	71	15514			

---

**Table 2 (continued).**

**Oxalate model: as separate Al<sub>ox</sub> and Fe<sub>ox</sub>**

	Parameter	Standard			
Variable	Estimate	Error	Type III SS	F Value	Pr > F
Intercept	0.76987	1.12702	12.33783	0.47	0.4968
Clay	0.06614	0.00491	4795.88580	181.38	<.0001
Alox	0.27414	0.01385	10365	392.02	<.0001

Bounds on condition number: 1.0141, 4.0563

All variables left in the model are significant at the 0.0001 level.

The stepwise method terminated because the next variable to be entered was just removed.

Summary of Stepwise Selection

Step	Variable Entered	Variable Removed	Number Vars In	Partial R-Square	Model R-Square	C(p)	F Value	Pr > F
1	Alox		1	0.5733	0.5733	196.772	94.04	<.0001
2	Clay		2	0.3091	0.8824	6.9649	181.38	<.0001
3	pH		3	0.0099	0.8923	2.8056	6.27	0.0147
4		pH	2	0.0099	0.8824	6.9649	6.27	0.0147

The REG Procedure

Model: MODEL1

Dependent Variable: Smax

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	13689	6844.74112	258.87	<.0001
Error	69	1824.39275	26.44047		
Corrected Total	71	15514			
Root MSE		5.14203	R-Square	0.8824	
Dependent Mean		21.87500	Adj R-Sq	0.8790	
Coeff Var		23.50642			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t	Standardized Estimate
Intercept	1	0.76987	1.12702	0.68	0.4968	0
Clay	1	0.06614	0.00491	13.47	<.0001	0.55990
Alox	1	0.27414	0.01385	19.80	<.0001	0.82312

**Table 3. The SAS output for stepwise regression of soil properties against  $S_{max}$  in the oxalate model as a single  $Al_{M3}$  and  $Fe_{M3}$ .**

---

**Mehlich-3 model: as a single variable of [ $Al_{M3}$  and  $Fe_{M3}$ ]**

---

Dependent Variable: Smax

Stepwise Selection: Step 1

Variable AIFEM3 Entered: R-Square = 0.7204 and C(p) = 105.6659

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	11176	11176	180.36	<.0001
Error	70	4337.64820	61.96640		
Corrected Total	71	15514			

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	-12.90796	2.75112	1364.11998	22.01	<.0001
AIFEM3	0.69547	0.05179	11176	180.36	<.0001

Bounds on condition number: 1, 1

Stepwise Selection: Step 2

Variable Clay Entered: R-Square = 0.8252 and C(p) = 42.5552

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	12802	6401.24793	162.90	<.0001
Error	69	2711.37914	39.29535		
Corrected Total	71	15514			

stepwise regression of M3 model with (Al+Fe)M3

The REG Procedure

Model: MODEL1

Dependent Variable: Smax

Stepwise Selection: Step 2

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	-15.69361	2.23318	1940.61714	49.39	<.0001
Clay	0.03881	0.00603	1626.26905	41.39	<.0001
AIFEM3	0.64986	0.04184	9478.22689	241.20	<.0001

Bounds on condition number: 1.0296, 4.1182

---



**Table 3 (continued).**

---

**Mehlich-3 model: as a single variable of [Al<sub>M3</sub> and Fe<sub>M3</sub>]**

---

Stepwise Selection: Step 3

Variable OM Entered: R-Square = 0.8888 and C(p) = 5.0801

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	13788	4596.15404	181.14	<.0001
Error	68	1725.41289	25.37372		
Corrected Total	71	15514			

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	-11.52486	1.91507	918.93976	36.22	<.0001
Clay	0.05119	0.00524	2423.02652	95.49	<.0001
OM	0.06496	0.01042	985.96625	38.86	<.0001
AIFEM3	0.45846	0.04553	2572.24984	101.37	<.0001

Bounds on condition number: 1.901, 14.975

All variables left in the model are significant at the 0.0001 level.

No other variable met the 0.1500 significance level for entry into the model.

stepwise regression of M3 model with (Al+Fe)M3

The REG Procedure

Model: MODEL1

Dependent Variable: Smax

Summary of Stepwise Selection

Step	Variable Entered	Variable Removed	Number of Variables in Model	Partial R-Square	Model R-Square	C(p)	F Value	Pr > F
1	AIFEM3		1	0.7204	0.7204	105.666	180.36	<.0001
2	Clay		2	0.1048	0.8252	42.5552	41.39	<.0001
3	OM		3	0.0636	0.8888	5.0801	38.86	<.0001

stepwise regression of M3 model with (Al+Fe)M3

---

**Table 3 (continued).**

---

**Mehlich-3 model: as a single variable of [Al<sub>M3</sub> and Fe<sub>M3</sub>]**

---

The REG Procedure

Model: MODEL1

Dependent Variable: Smax

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	13788	4596.15404	181.14	<.0001
Error	68	1725.41289	25.37372		
Corrected Total	71	15514			
	Root MSE	5.03723	R-Square	0.8888	
	Dependent Mean	21.87500	Adj R-Sq	0.8839	
	Coeff Var	23.02735			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t	Standardized Estimate
Intercept	1	-11.52486	1.91507	-6.02	<.0001	0
Clay	1	0.05119	0.00524	9.77	<.0001	0.43339
OM	1	0.06496	0.01042	6.23	<.0001	0.34758
AIFEM3	1	0.45846	0.04553	10.07	<.0001	0.55951

---

**Table 4. The SAS output for stepwise regression of soil properties against  $S_{max}$  in the Mehlich-3 model as separate  $Al_{M3}$  and  $Fe_{M3}$ .**

---

**Mehlich-3 model: as separate  $Al_{M3}$  and  $Fe_{M3}$**

---

The REG Procedure  
 Model: MODEL1  
 Dependent Variable: Smax  
 Stepwise Selection: Step 1  
 Variable AIM3 Entered: R-Square = 0.7427 and C(p) = 97.8201

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	11522	11522	202.03	<.0001
Error	70	3992.09196	57.02989		
Corrected Total	71	15514			

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	-13.00683	2.61049	1415.80125	24.83	<.0001
AIM3	0.73911	0.05200	11522	202.03	<.0001

Bounds on condition number: 1, 1

---

Stepwise Selection: Step 2  
 Variable Clay Entered: R-Square = 0.8235 and C(p) = 47.7498

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	12775	6387.68389	160.95	<.0001
Error	69	2738.50722	39.68851		
Corrected Total	71	15514			

Dependent Variable: Smax  
 Stepwise Selection: Step 2

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	-14.96295	2.20536	1827.00279	46.03	<.0001
Clay	0.03438	0.00612	1253.58474	31.59	<.0001
AIM3	0.68544	0.04442	9451.09881	238.13	<.0001

Bounds on condition number: 1.0485, 4.1939

---

**Table 4 (continued).**

---

**Mehlich-3 model: as separate Al<sub>M3</sub> and Fe<sub>M3</sub>**

---

Stepwise Selection: Step 3

Variable OM Entered: R-Square = 0.8960 and C(p) = 3.0311

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	13900	4633.37093	195.24	<.0001
Error	68	1613.76220	23.73180		
Corrected Total	71	15514			

Variable	Parameter Estimate	Standard Error	Type III SS	F Value	Pr > F
Intercept	-11.13317	1.79379	914.16507	38.52	<.0001
Clay	0.04843	0.00515	2097.24075	88.37	<.0001
OM	0.06760	0.00982	1124.74502	47.39	<.0001
AlM3	0.48192	0.04532	2683.90054	113.09	<.0001

Bounds on condition number: 1.8251, 14.62

All variables left in the model are significant at the 0.0001 level.

No other variable met the 0.1500 significance level for entry into the model.

stepwise regression of M3 model with Al and Fe separately

The REG Procedure

Model: MODEL1

Dependent Variable: Smax

Summary of Stepwise Selection

Step	Variable Entered	Variable Removed	Number of Variables in Model	Partial R-Square	Model R-Square	C(p)	F Value	Pr > F
1	AlM3		1	0.7427	0.7427	97.8201	202.03	<.0001
2	Clay		2	0.0808	0.8235	47.7498	31.59	<.0001
3	OM		3	0.0725	0.8960	3.0311	47.39	<.0001

stepwise regression of M3 model with Al and Fe separately

---

**Table 4 (continued).****Mehlich-3 model: as separate Al<sub>M3</sub> and Fe<sub>M3</sub>**

The REG Procedure

Model: MODEL1

Dependent Variable: Smax

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	13900	4633.37093	195.24	<.0001
Error	68	1613.76220	23.73180		
Corrected Total	71	15514			
	Root MSE	4.87153	R-Square	0.8960	
	Dependent Mean	21.87500	Adj R-Sq	0.8914	
	Coeff Var	22.26985			

Parameter Estimates

Variable	DF	Parameter Estimate	Standard Error	t Value	Pr >  t	Standardized Estimate
Intercept	1	-11.13317	1.79379	-6.21	<.0001	0
Clay	1	0.04843	0.00515	9.40	<.0001	0.41003
OM	1	0.06760	0.00982	6.88	<.0001	0.36169
AlM3	1	0.48192	0.04532	10.63	<.0001	0.56191

**Table 5. Significance test in the regression slopes of  $S_{max}$  against  $[Al_{ox}+Fe_{ox}]$  by soil types.**

**Variables: OxAlFe =  $[Al_{ox}+Fe_{ox}]$  and group = mineral or mineral-organic soils**

The SAS System

The GLM Procedure

Dependent Variable: Smax

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	2	44938.82031	22469.41016	312.81	<.0001
Error	70	5028.17969	71.83114		
Uncorrected Total	72	49967.00000			

R-Square      Coeff Var      Root MSE      Smax Mean  
 0.675891      38.74434      8.475325      21.87500

Source	DF	Type I SS	Mean Square	F Value	Pr > F
OxAlFe	1	41307.99070	41307.99070	575.07	<.0001
OxAlFe*group	1	3630.82961	3630.82961	50.55	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
OxAlFe	1	21091.59608	21091.59608	293.63	<.0001
OxAlFe*group	1	3630.82961	3630.82961	50.55	<.0001

**Table 6. Segmented regression of organic matter against P sorption maximum ( $S_{max}$ ).**

**Dependant variable =  $S_{max}$ , predictive variable = OM by mineral or mineral-organic**

The NLIN Procedure

Dependent Variable S					
Method: Gauss-Newton					
Iterative Phase					
Iter	a	x0	b	d	Sum of Squares
0	0	50.0000	0.7500	0.0500	5568.0
1	-2.4407	43.4528	0.7477	0.0514	4299.6
2	-2.3601	45.1386	0.7421	0.0468	4289.9
3	-2.6089	44.1359	0.7582	0.0478	4286.8
4	-2.6089	44.1572	0.7582	0.0478	4286.8

NOTE: Convergence criterion met.

Estimation Summary					
Method	Gauss-Newton				
Iterations	4				
R	0				
PPC	0				
RPC(x0)	0.000481				
Object	1.435E-6				
Objective	4286.811				
Observations Read	72				
Observations Used	72				
Observations Missing	0				
Source	DF	Sum of Squares	Mean Square	F Value	Approx Pr > F
Regression	4	45680.2	11420.0	59.36	<.0001
Residual	68	4286.8	63.0413		
Uncorrected Total	72	49967.0			
Corrected Total	71	15513.9			
Parameter	Estimate	Std Error	Approximate 95% Confidence Limits		
a	-2.6089	2.4862	-7.5700	2.3522	
x0	42.1572	4.3357	35.5054	52.8090	
b	0.7582	0.0977	0.5632	0.9532	
d	0.0478	0.0149	0.0180	0.0776	

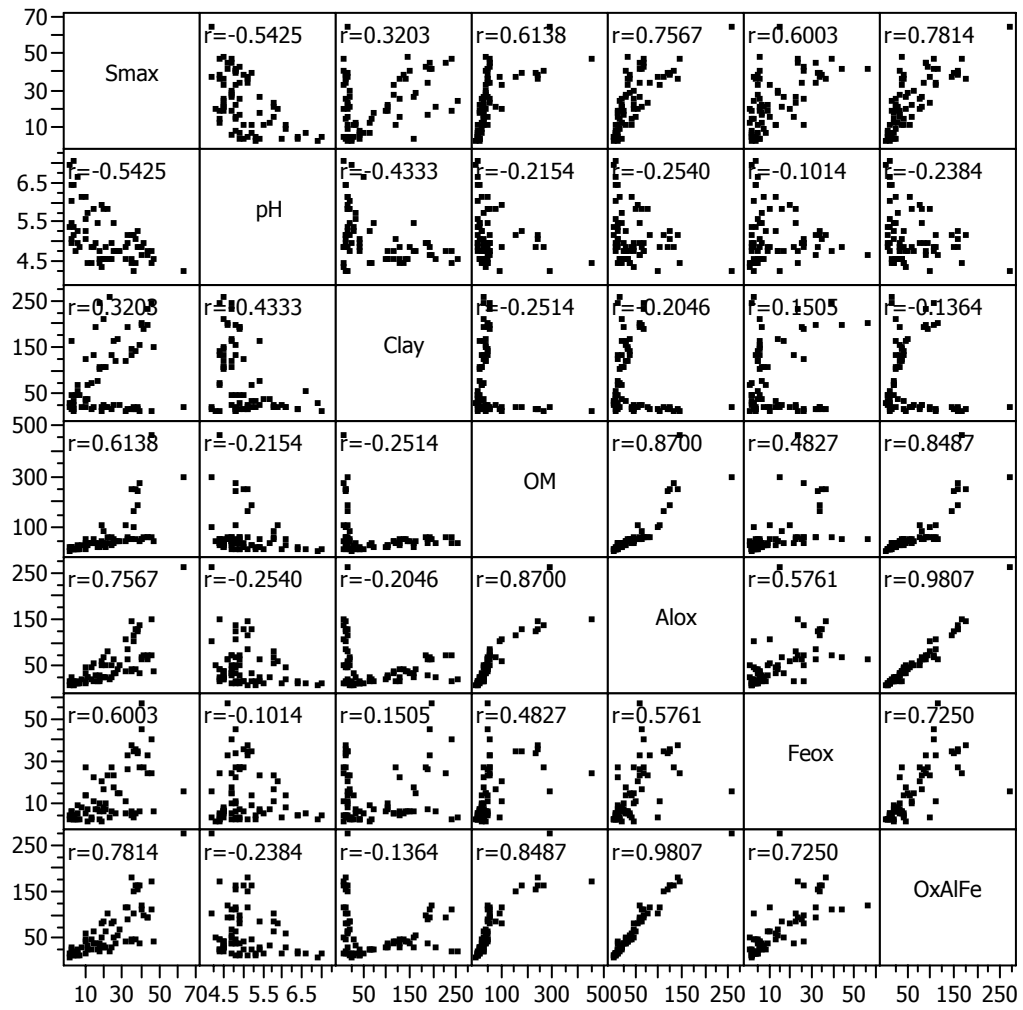
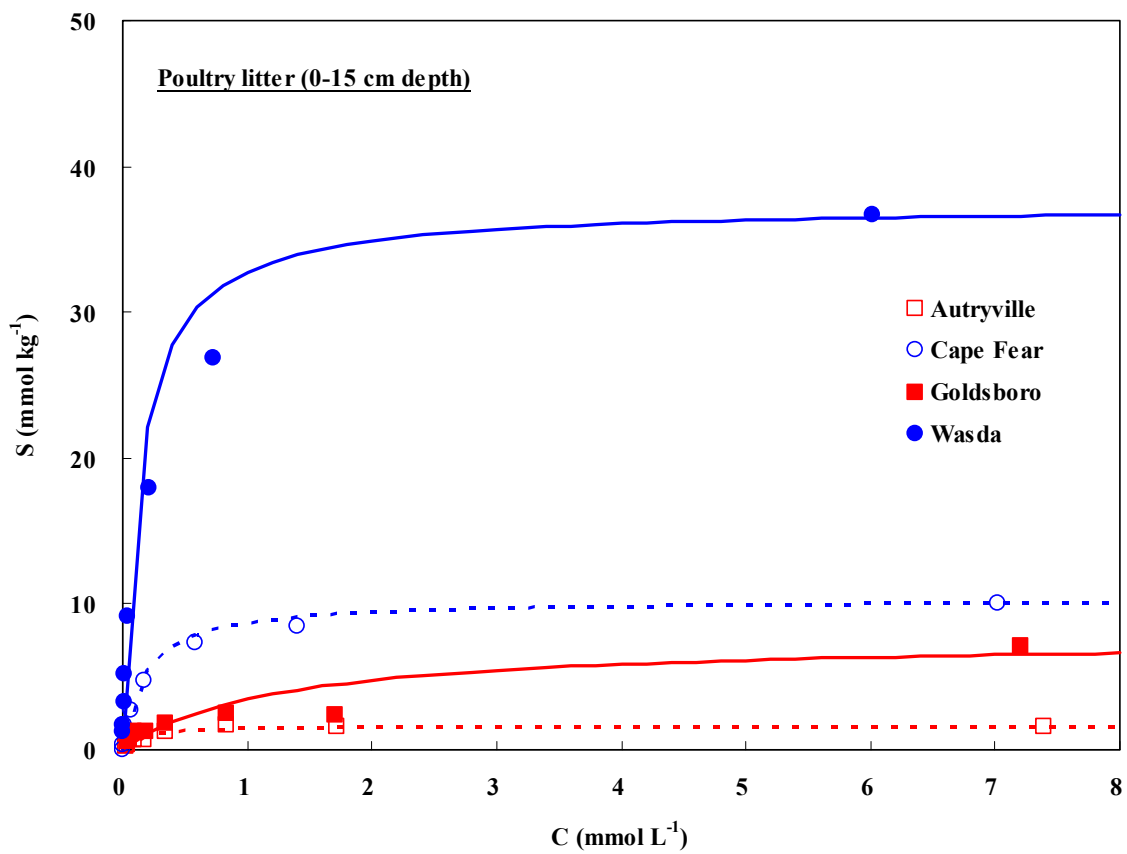
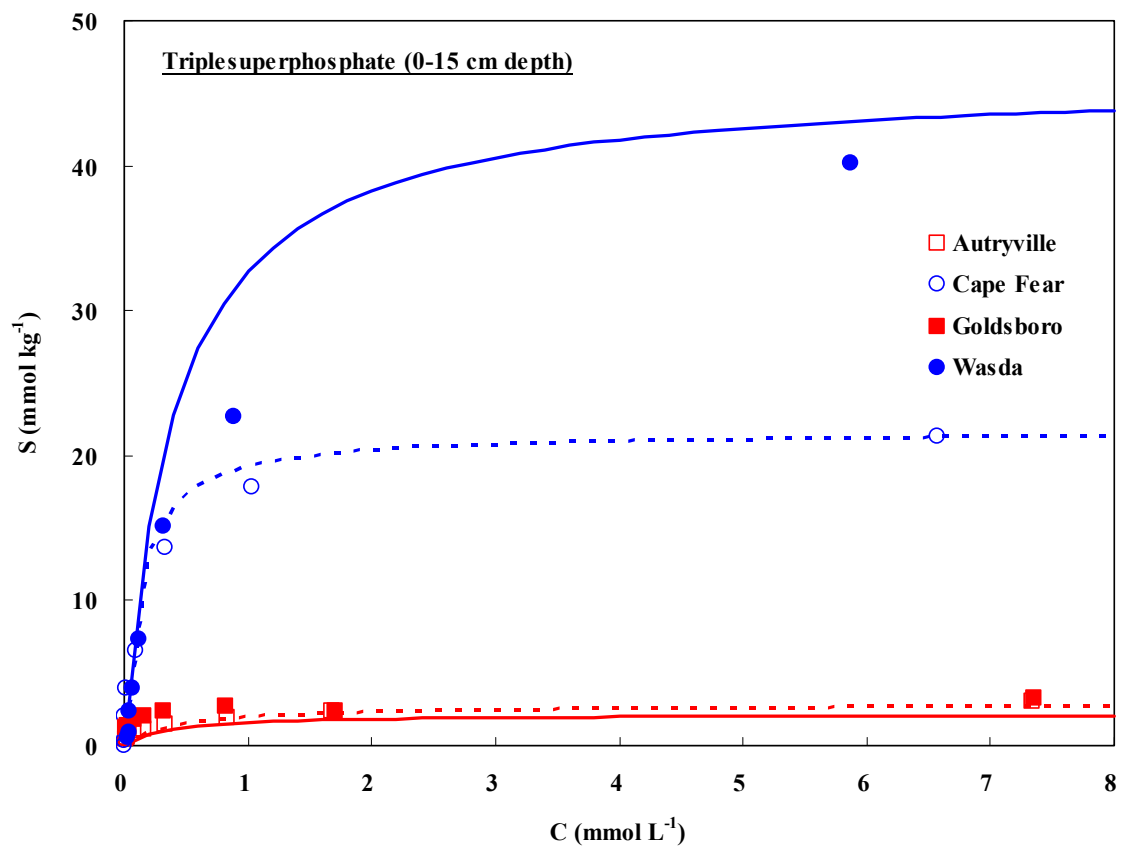
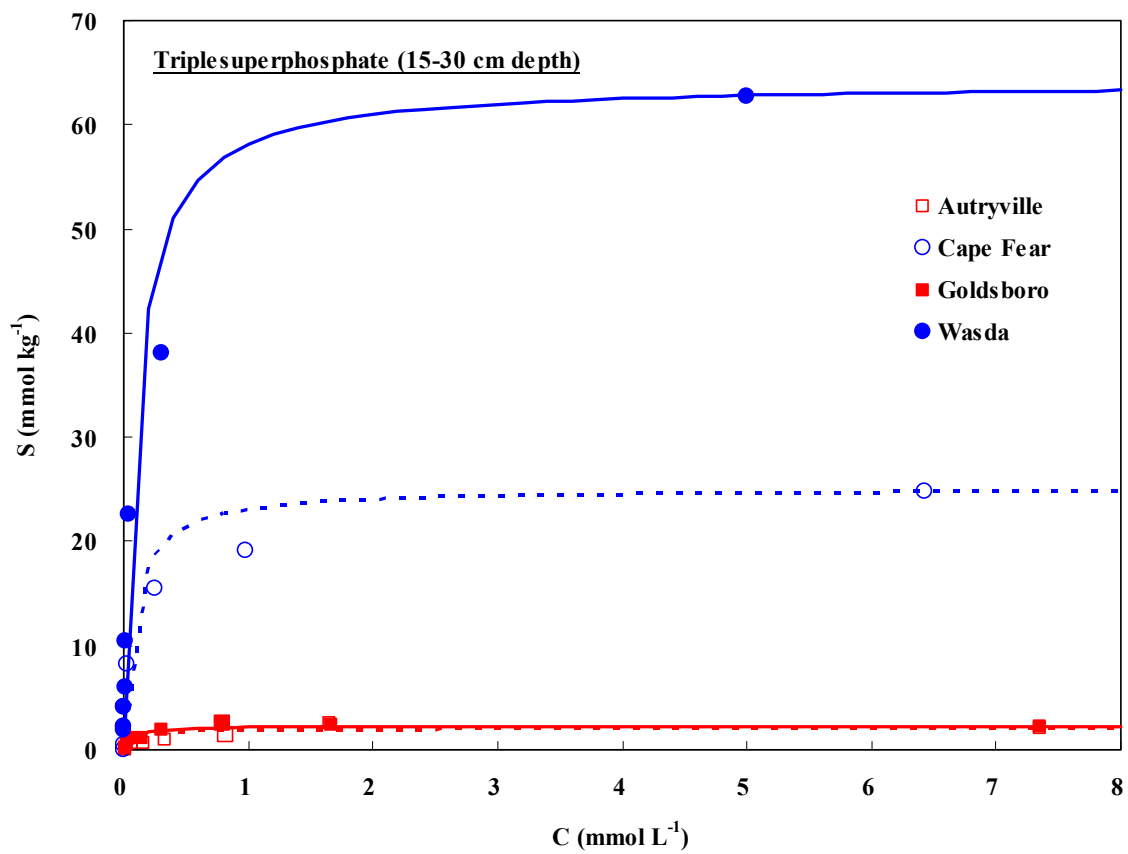
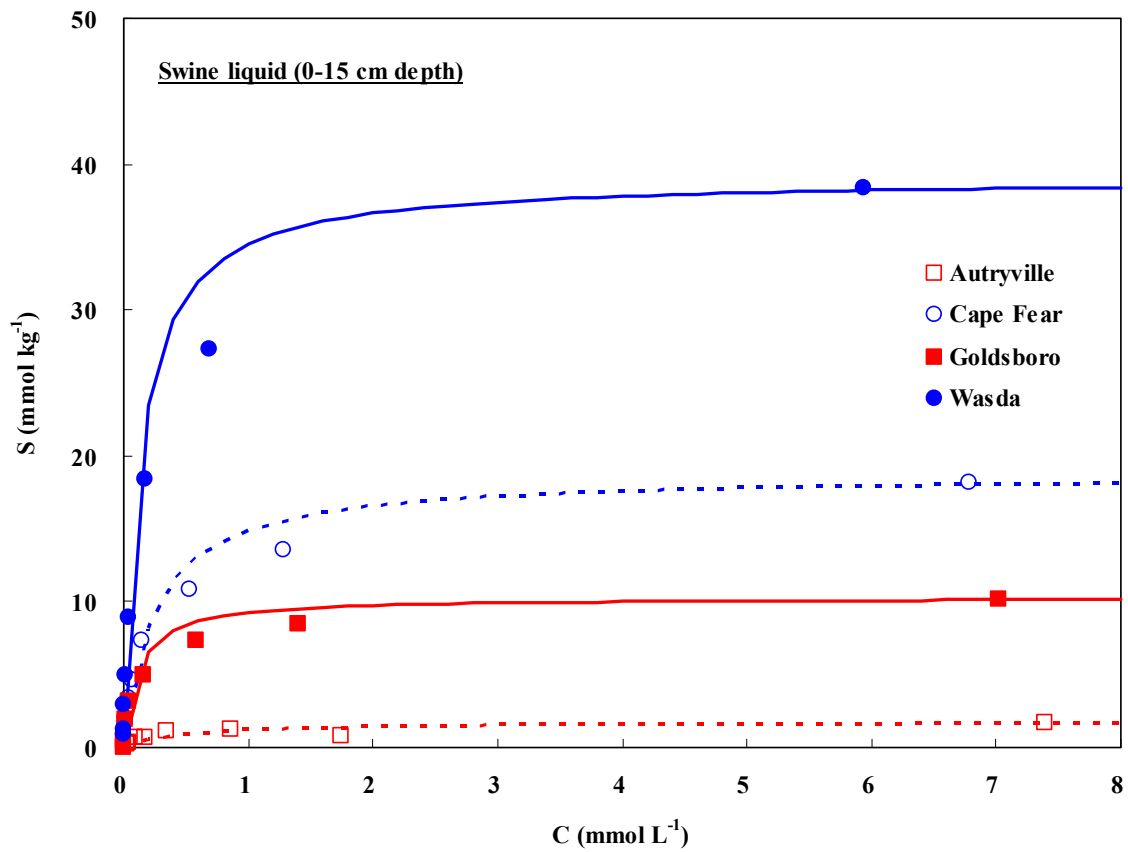


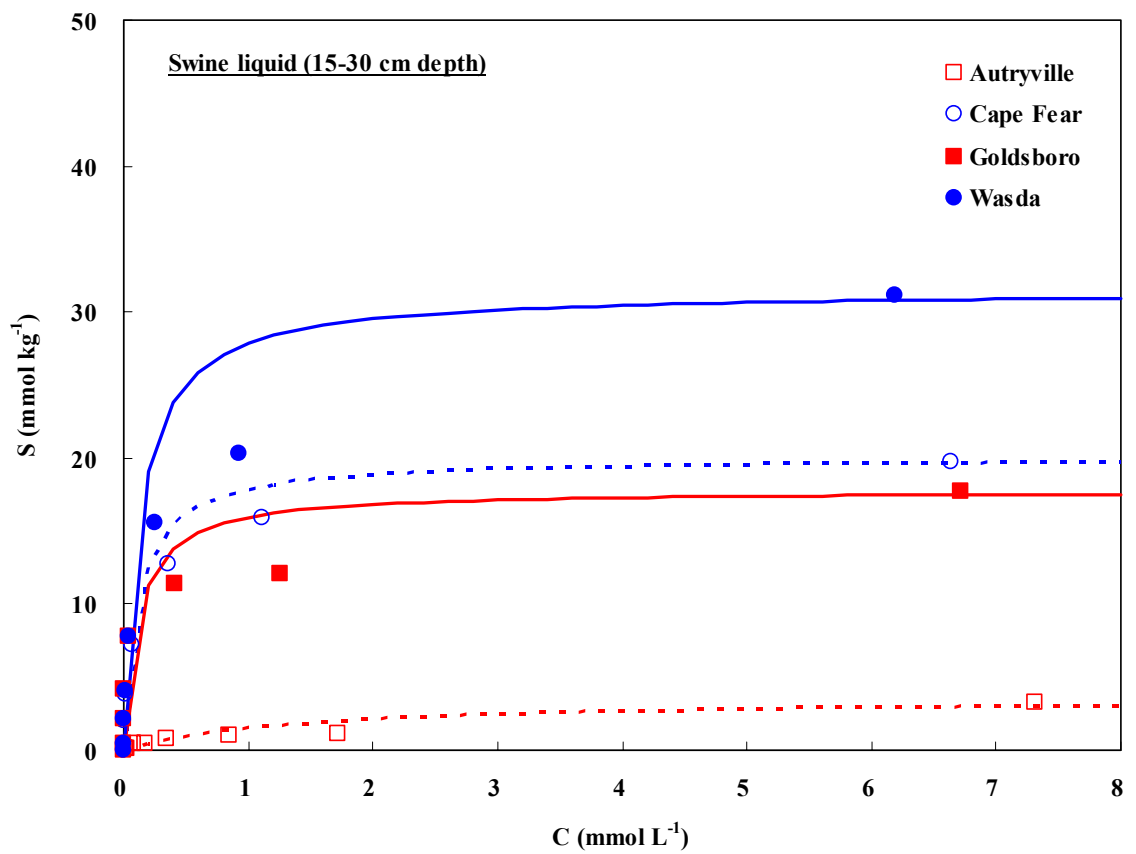
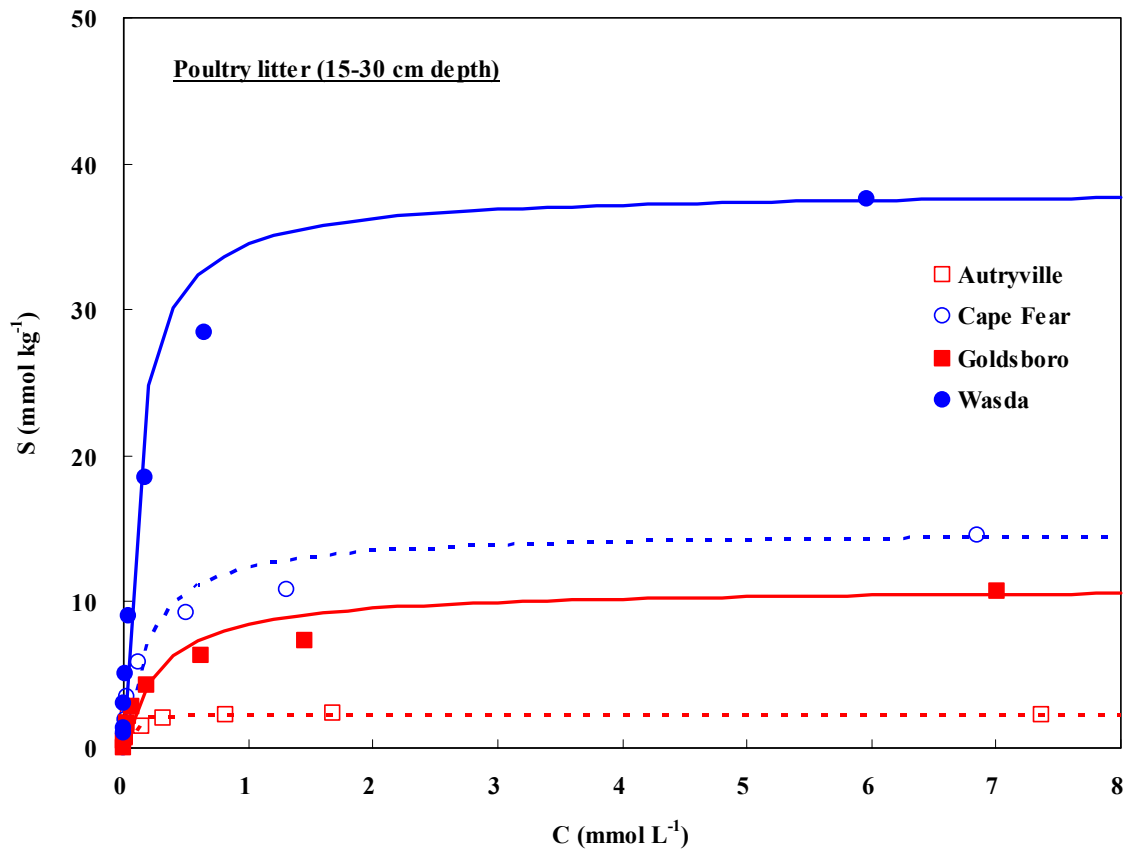
Figure 1. Scatter plot between P sorption maximum ( $S_{max}$ ) and soil properties (pH, clay, OM,  $Al_{ox}$ ,  $Fe_{ox}$  and  $[Al_{ox}+Fe_{ox}]$ ).

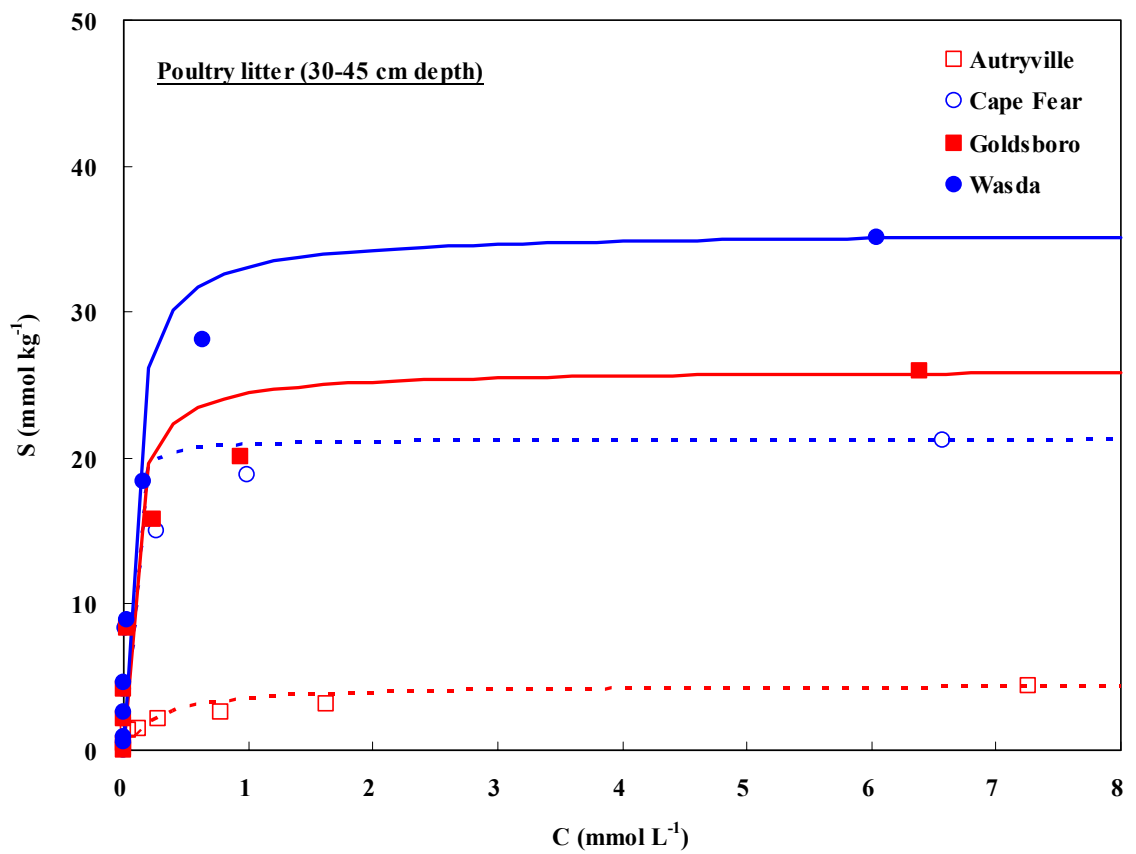
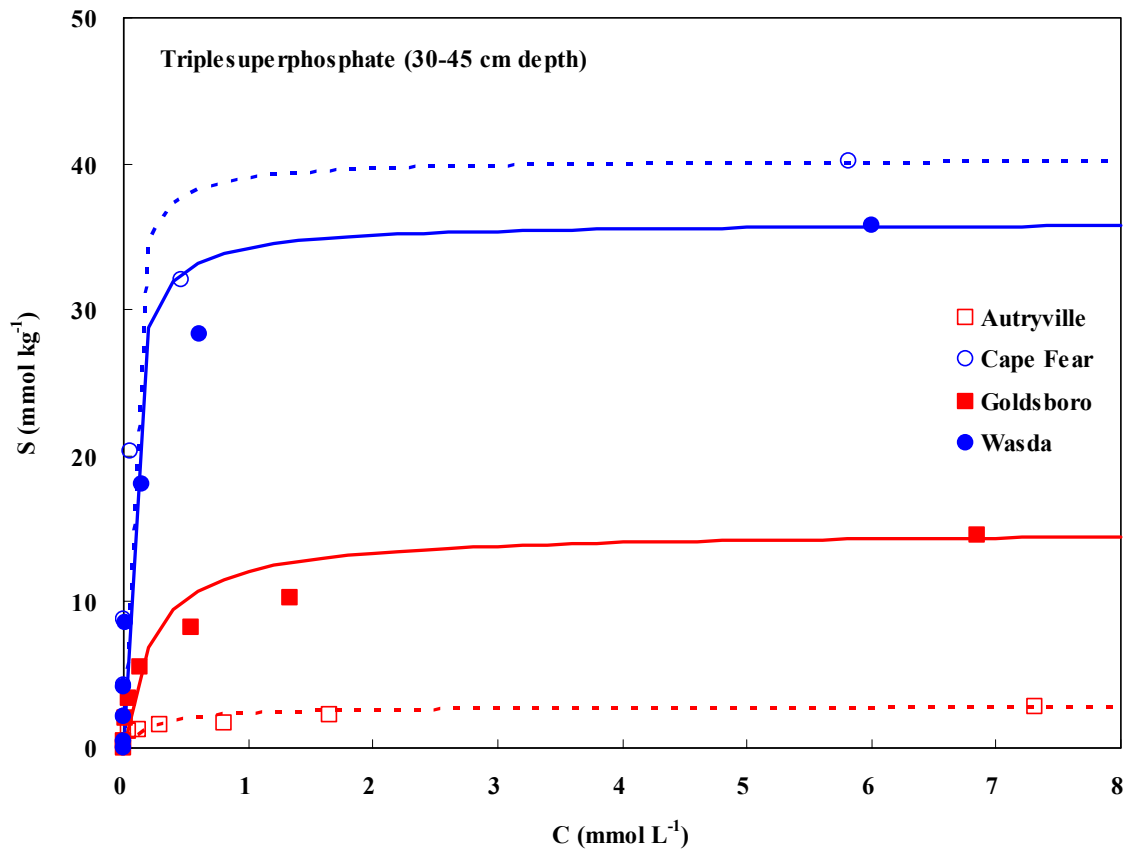


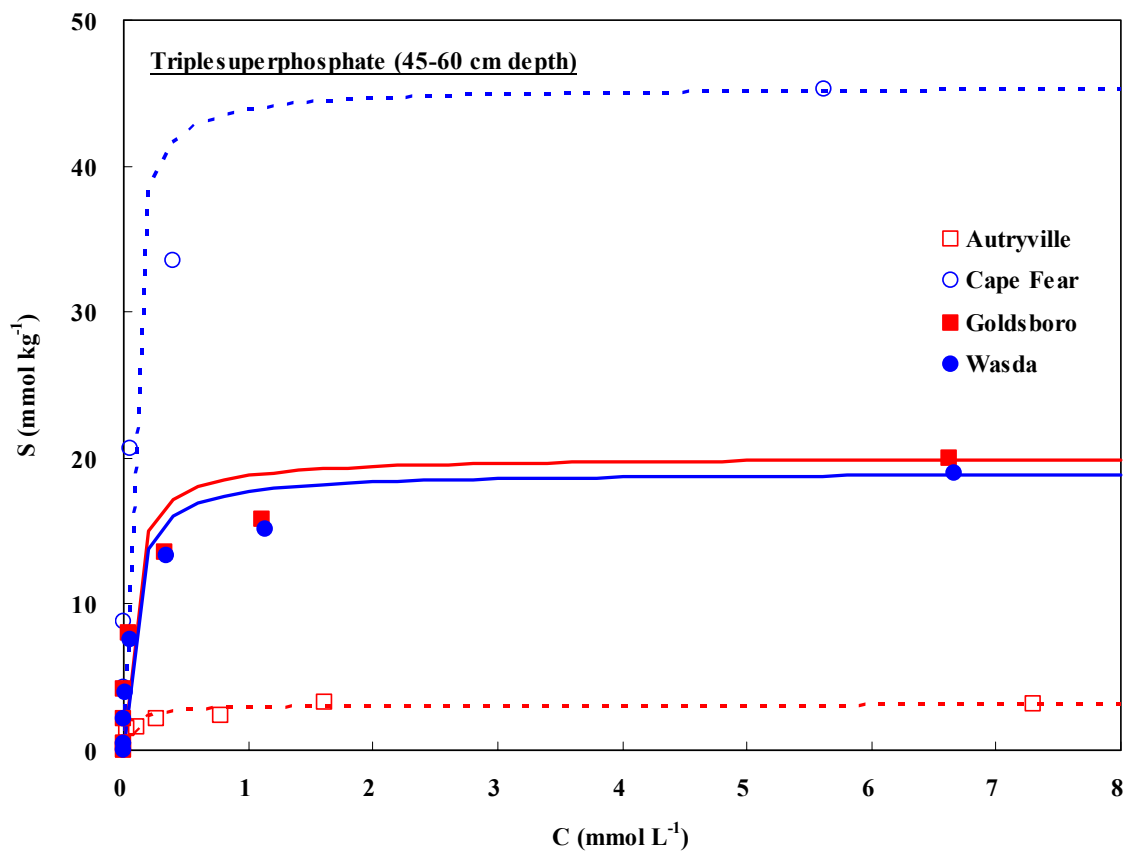
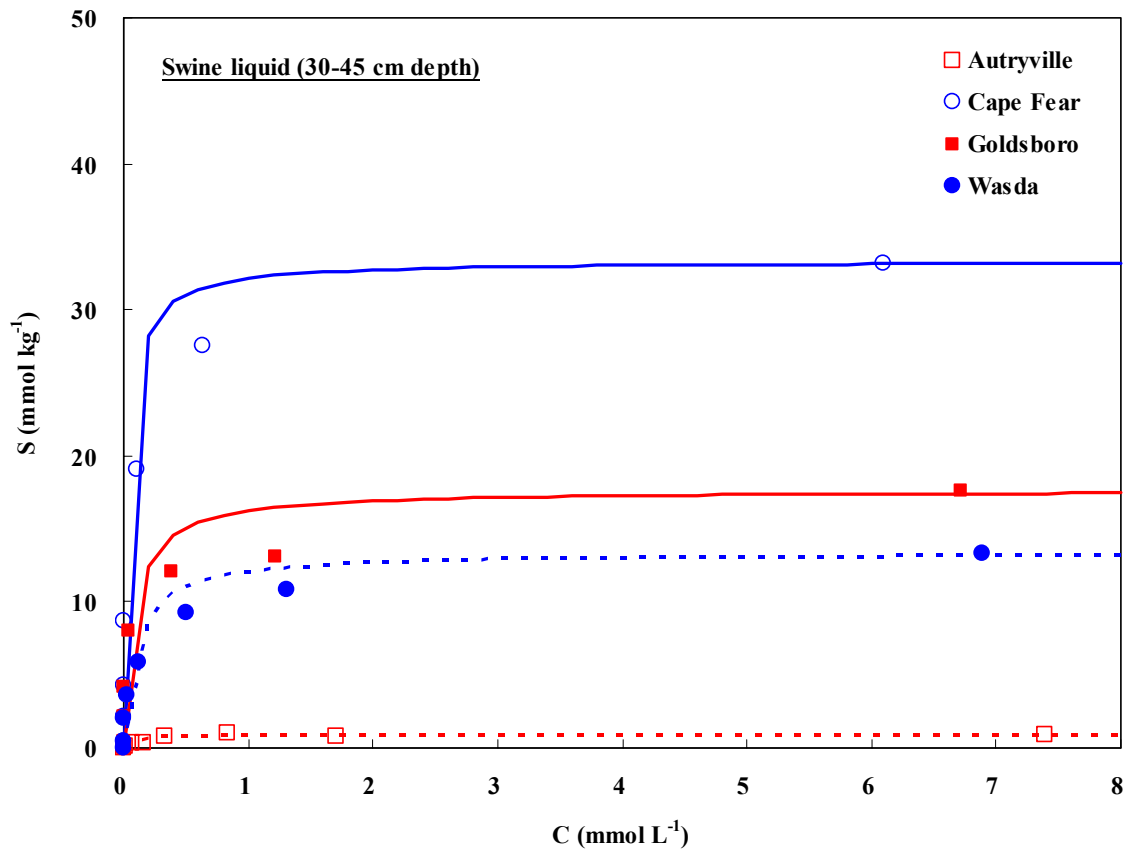
**Figure 2. Phosphorus sorption isotherms plotted according to the Langmuir equation. The sorption data were organized by fertilizer histories (triplesuperphosphate, poultry litter, and swine liquid) and sampling depths (0-15, 15-30, 30-45, 45-60, 60-75, and 75-90 cm depth).**

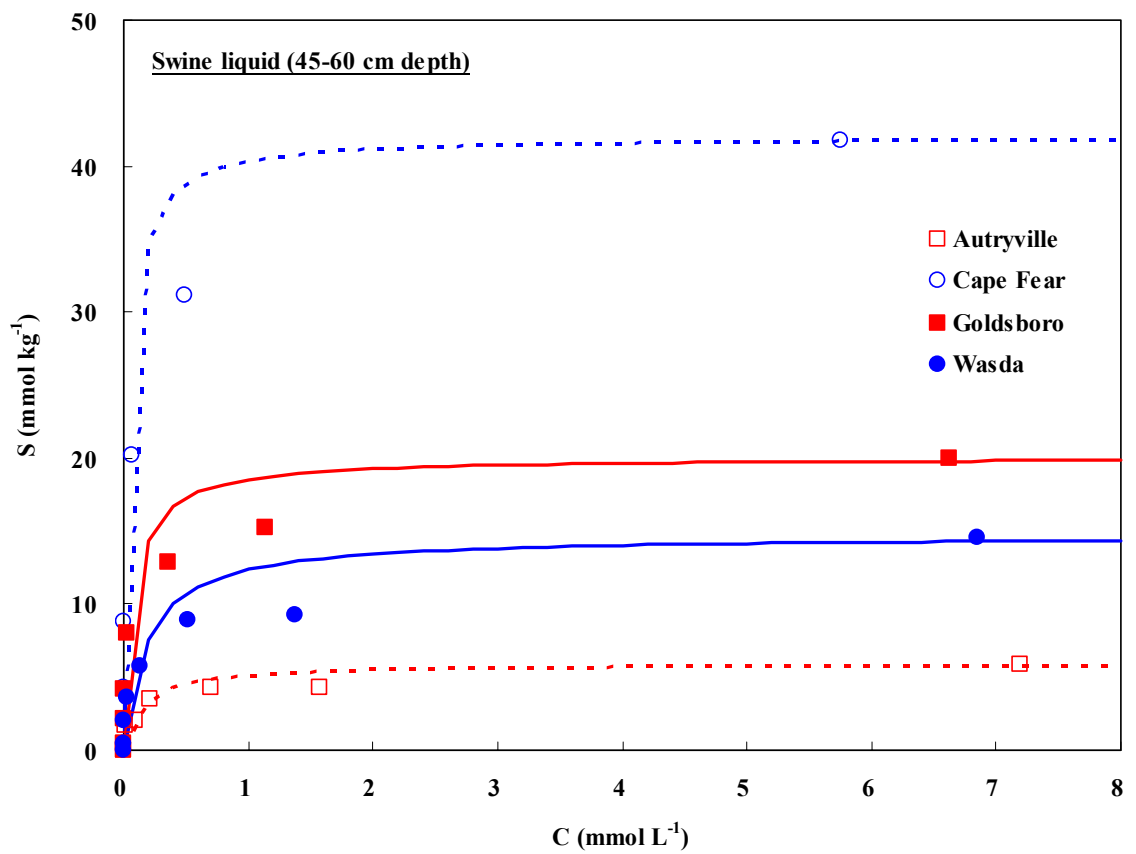
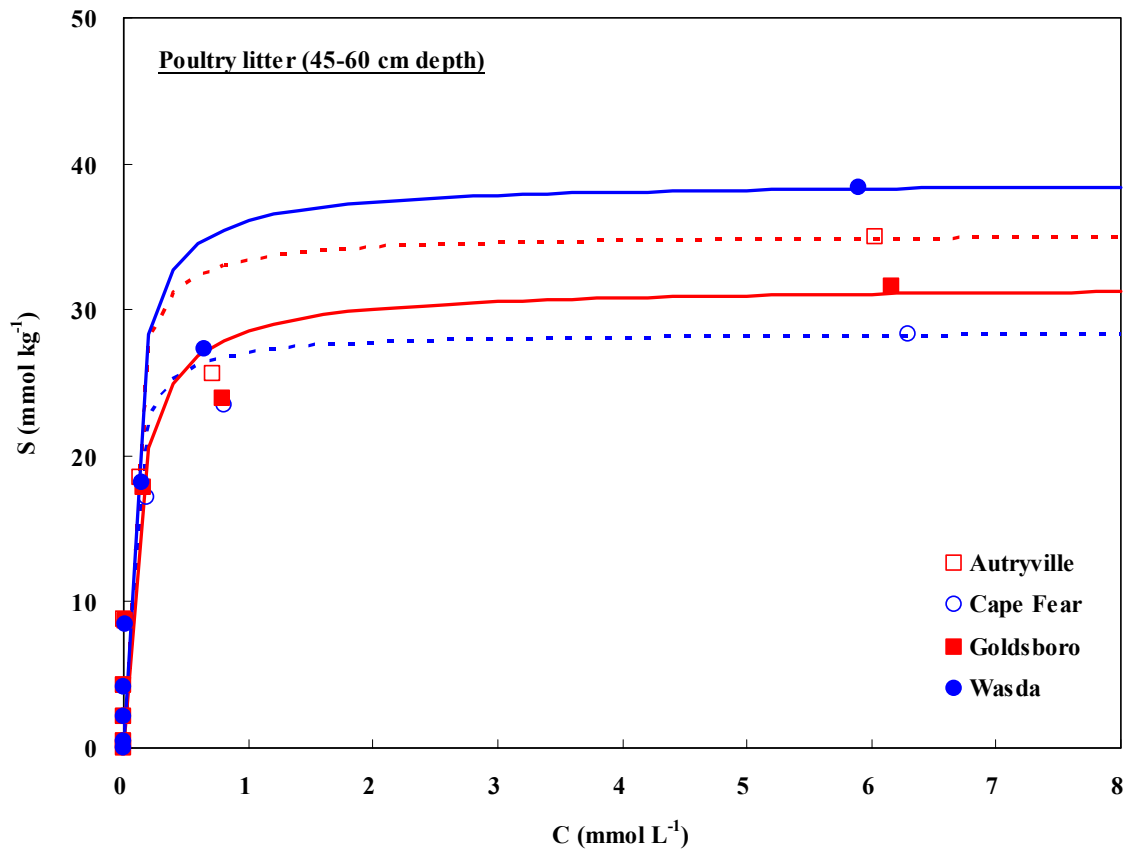


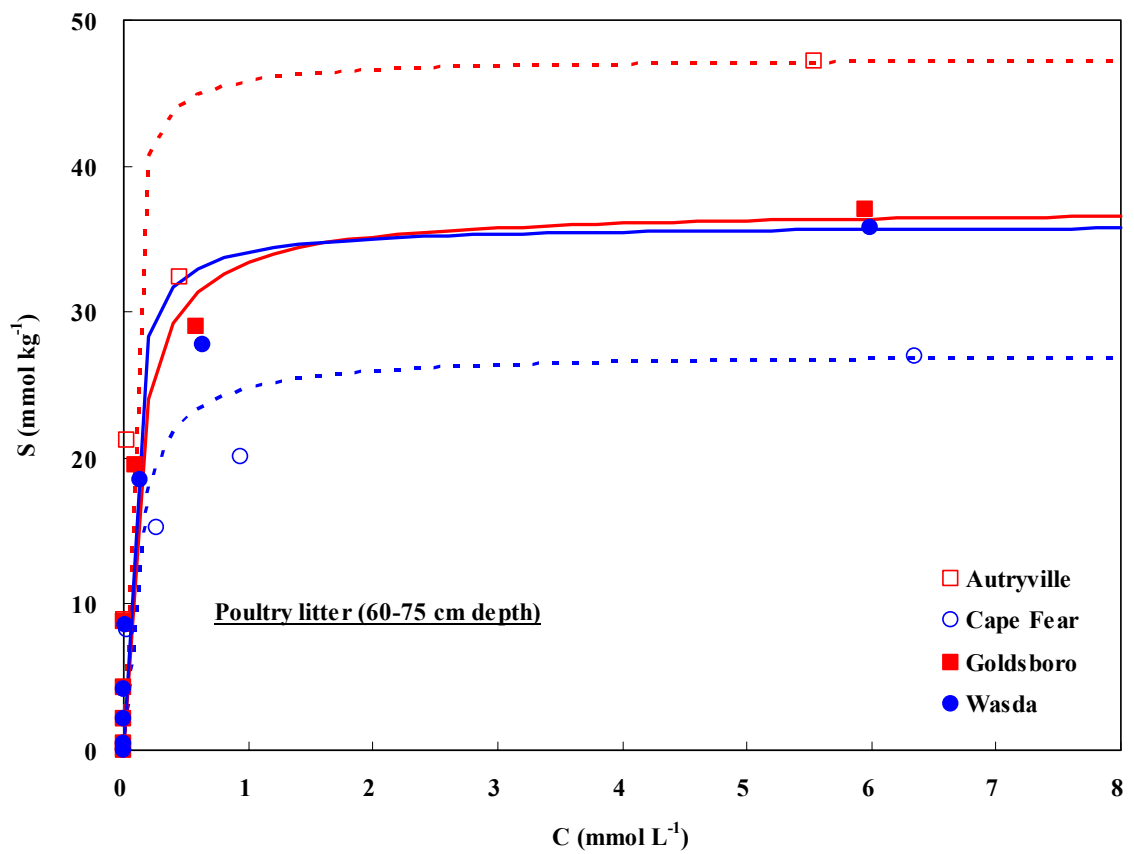
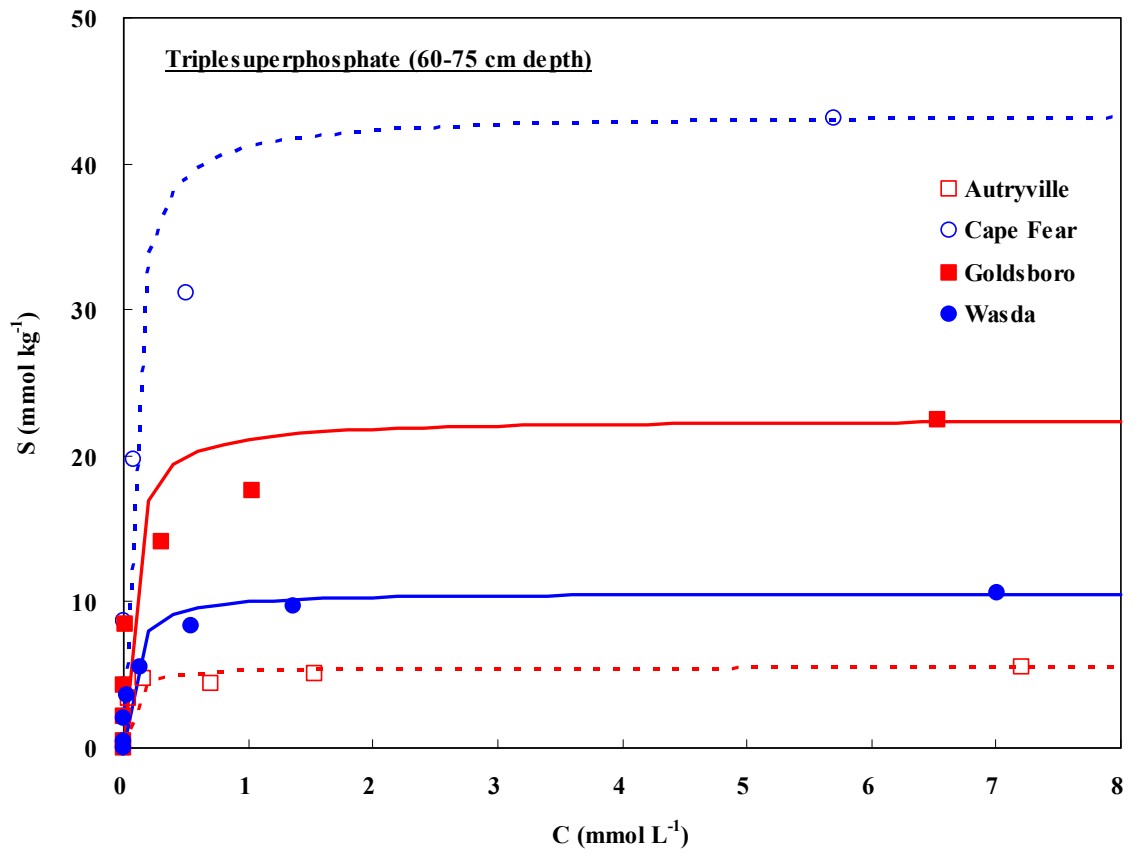




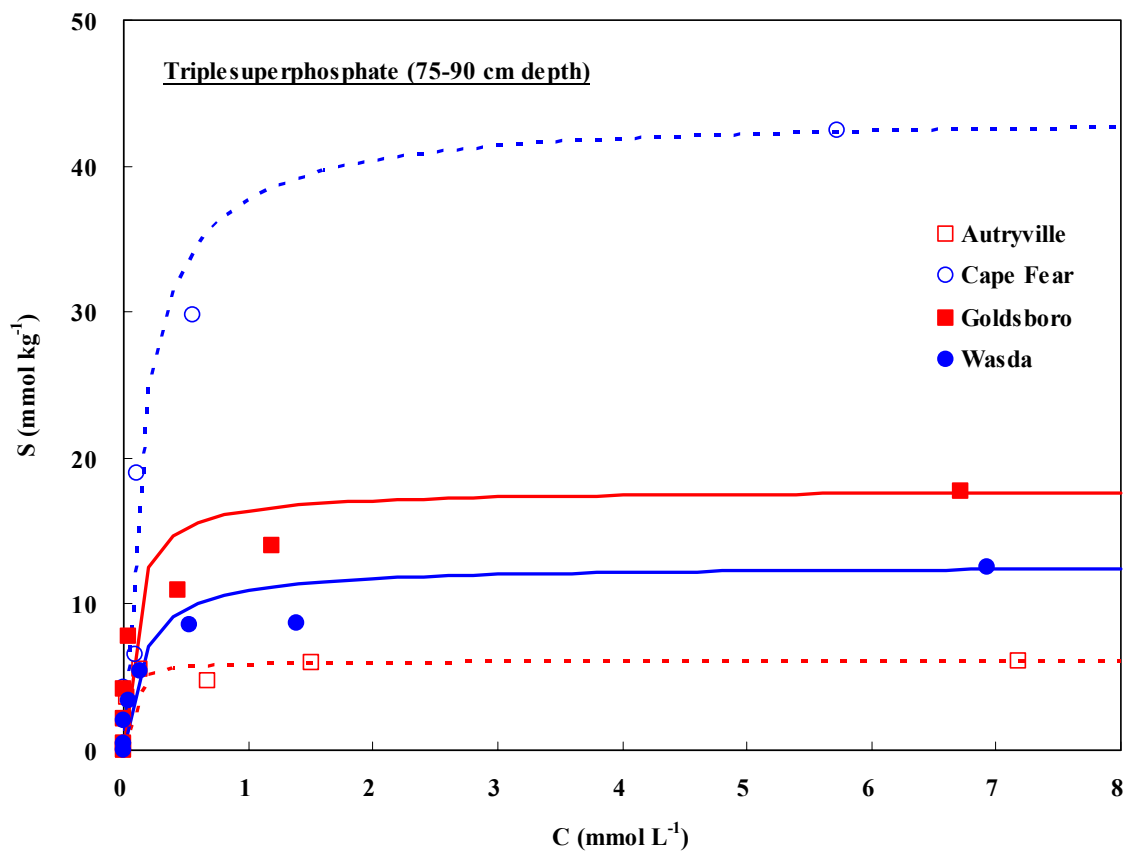
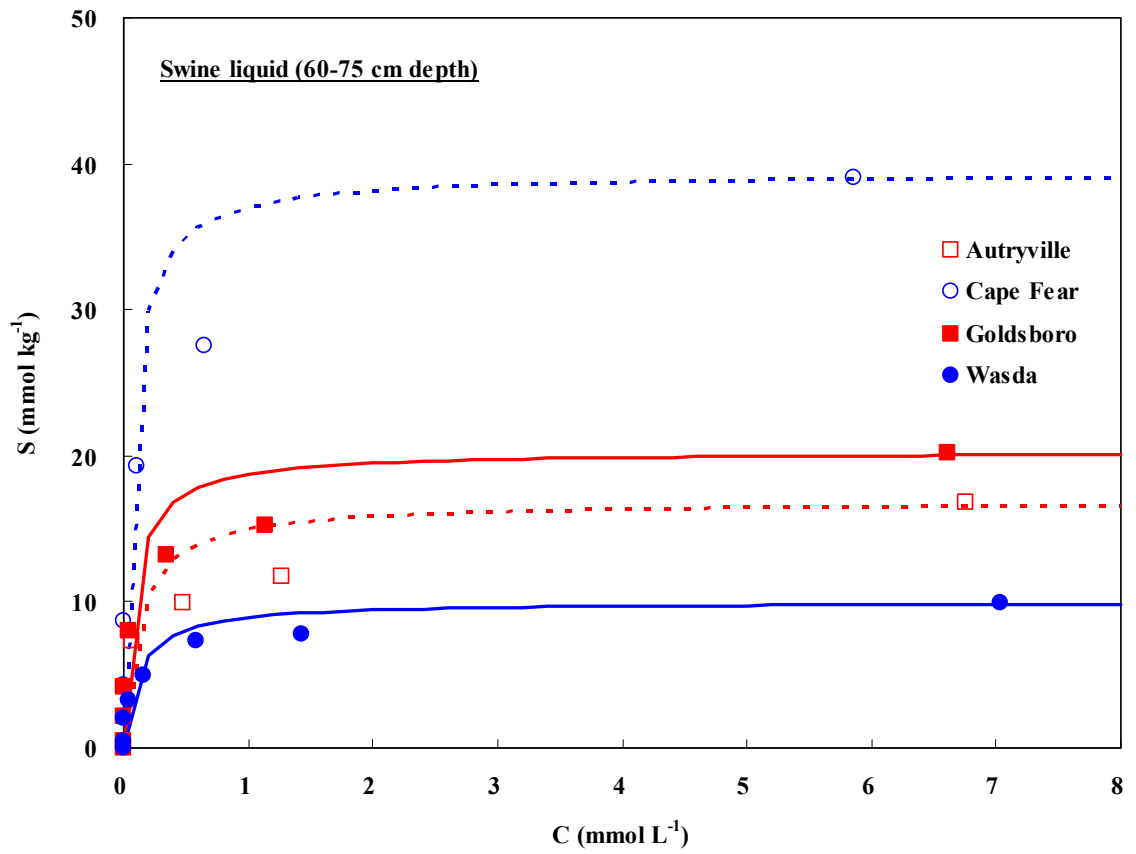


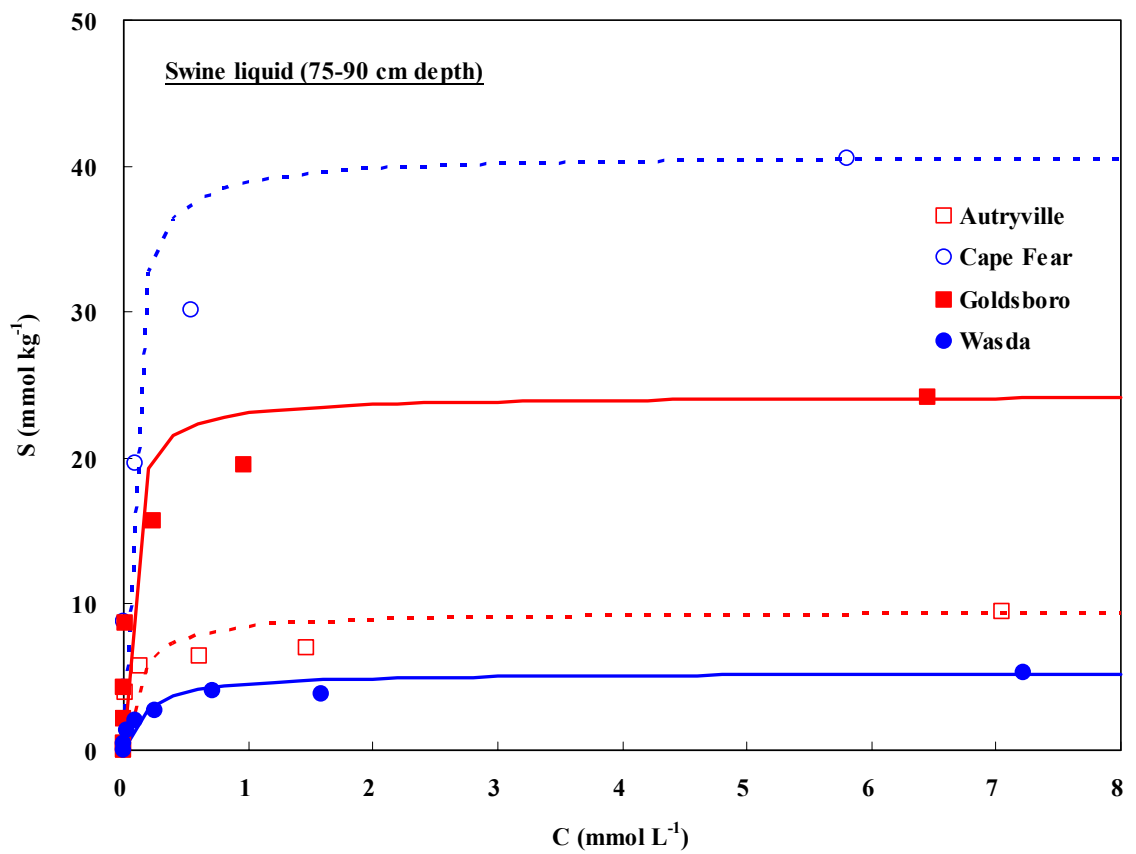
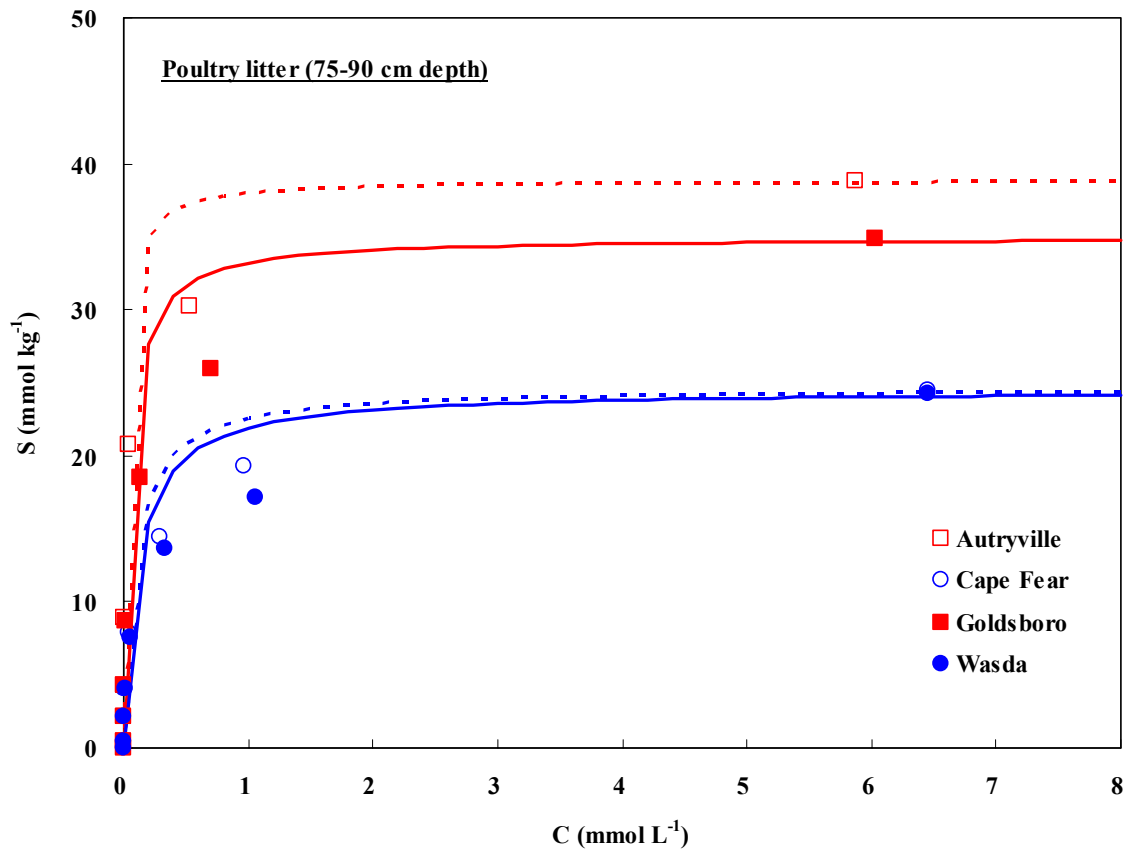












## Appendix B. Supporting materials for chapter 2

**Table 1. Peak concentration of DRP and DOC from columns treated with P mixtures.**

P source mixture <sup>†</sup>	P load kg TP ha <sup>-1</sup>	Pulse duration	Peak DRP			Peak DOC		
			PV <sup>††</sup>	DRP mg L <sup>-1</sup>	SE <sup>§</sup>	PV	DOC mg L <sup>-1</sup>	SE
DL	150 (high)	6.92	9	21	1.4	3	190	2.0
SL		6.92	11	23	1.4	4	136	2.6
KP		6.8	7	47	0.8	4	15	1.2
PC		2	5	19	0.6	2	263	1.2
PL		2	5	19	0.6	2	287	4.5
SS		2	5	22	1.8	4	48	2.5
TSP		2	3	68	6.0	2	30	2.8
DL	75 (medium)	3.46	7	11	1.8	2	179	3.9
SL		3.46	7	13	2.1	3	178	7.2
KP		3.4	4	39	1.6	4	16	1.2
PC		2	5	8	0.3	3	157	3.7
PL		2	5	9	1.2	3	137	7.4
SS		2	7	5	0.2	4	29	3.0
TSP		2	4	34	1.8	3	19	0.4

<sup>†</sup> DL, dairy liquid; PC, poultry compost; PL, poultry litter; SL, swine liquid; SS, swine sludge; KP, dissolved KH<sub>2</sub>PO<sub>4</sub>; TSP, triplesuperphosphate.

<sup>††</sup> Number of pore volume leached.

<sup>§</sup> Standard error

**Table 2. The CXTFIT-fitted P transport data following one-dimensional convection-dispersion equation with dissolved  $\text{KH}_2\text{PO}_4$ .**

PV	C/C <sub>0</sub>	PV	C/C <sub>0</sub>	PV	C/C <sub>0</sub>	PV	C/C <sub>0</sub>	PV	C/C <sub>0</sub>
0	1.75E-02								
0.1	1.75E-02	5.1	3.25E-01	10.1	9.42E-01	15.1	1.44E-01	20.1	3.80E-03
0.2	1.75E-02	5.2	3.48E-01	10.2	9.39E-01	15.2	1.35E-01	20.2	3.52E-03
0.3	1.75E-02	5.3	3.70E-01	10.3	9.35E-01	15.3	1.27E-01	20.3	3.25E-03
0.4	1.75E-02	5.4	3.93E-01	10.4	9.30E-01	15.4	1.19E-01	20.4	3.00E-03
0.5	1.75E-02	5.5	4.16E-01	10.5	9.23E-01	15.5	1.11E-01	20.5	2.77E-03
0.6	1.75E-02	5.6	4.38E-01	10.6	9.15E-01	15.6	1.04E-01	20.6	2.56E-03
0.7	1.75E-02	5.7	4.61E-01	10.7	9.06E-01	15.7	9.75E-02	20.7	2.37E-03
0.8	1.75E-02	5.8	4.83E-01	10.8	8.95E-01	15.8	9.12E-02	20.8	2.19E-03
0.9	1.75E-02	5.9	5.05E-01	10.9	8.83E-01	15.9	8.53E-02	20.9	2.02E-03
1	1.75E-02	6	5.26E-01	11	8.70E-01	16	7.97E-02	21	1.86E-03
1.1	1.75E-02	6.1	5.47E-01	11.1	8.55E-01	16.1	7.45E-02	21.1	1.72E-03
1.2	1.75E-02	6.2	5.68E-01	11.2	8.39E-01	16.2	6.96E-02	21.2	1.59E-03
1.3	1.75E-02	6.3	5.88E-01	11.3	8.23E-01	16.3	6.49E-02	21.3	1.47E-03
1.4	1.75E-02	6.4	6.08E-01	11.4	8.05E-01	16.4	6.06E-02	21.4	1.35E-03
1.5	1.75E-02	6.5	6.27E-01	11.5	7.86E-01	16.5	5.65E-02	21.5	1.25E-03
1.6	1.75E-02	6.6	6.45E-01	11.6	7.67E-01	16.6	5.27E-02	21.6	1.15E-03
1.7	1.75E-02	6.7	6.63E-01	11.7	7.46E-01	16.7	4.91E-02	21.7	1.06E-03
1.8	1.75E-02	6.8	6.81E-01	11.8	7.25E-01	16.8	4.57E-02	21.8	9.80E-04
1.9	1.76E-02	6.9	6.97E-01	11.9	7.04E-01	16.9	4.26E-02	21.9	9.04E-04
2	1.76E-02	7	7.13E-01	12	6.82E-01	17	3.97E-02	22	8.34E-04
2.1	1.77E-02	7.1	7.29E-01	12.1	6.60E-01	17.1	3.69E-02	22.1	7.69E-04
2.2	1.79E-02	7.2	7.44E-01	12.2	6.37E-01	17.2	3.43E-02	22.2	7.09E-04
2.3	1.81E-02	7.3	7.58E-01	12.3	6.15E-01	17.3	3.19E-02	22.3	6.54E-04
2.4	1.86E-02	7.4	7.71E-01	12.4	5.92E-01	17.4	2.97E-02	22.4	6.03E-04
2.5	1.93E-02	7.5	7.84E-01	12.5	5.70E-01	17.5	2.76E-02	22.5	5.56E-04
2.6	2.02E-02	7.6	7.97E-01	12.6	5.47E-01	17.6	2.57E-02	22.6	5.12E-04
2.7	2.16E-02	7.7	8.09E-01	12.7	5.25E-01	17.7	2.38E-02	22.7	4.72E-04
2.8	2.34E-02	7.8	8.20E-01	12.8	5.03E-01	17.8	2.21E-02	22.8	4.35E-04
2.9	2.58E-02	7.9	8.31E-01	12.9	4.82E-01	17.9	2.06E-02	22.9	4.01E-04
3	2.89E-02	8	8.41E-01	13	4.61E-01	18	1.91E-02	23	3.70E-04
3.1	3.27E-02	8.1	8.50E-01	13.1	4.40E-01	18.1	1.77E-02	23.1	3.41E-04
3.2	3.74E-02	8.2	8.60E-01	13.2	4.19E-01	18.2	1.64E-02	23.2	3.14E-04
3.3	4.31E-02	8.3	8.68E-01	13.3	4.00E-01	18.3	1.52E-02	23.3	2.89E-04
3.4	4.98E-02	8.4	8.76E-01	13.4	3.80E-01	18.4	1.41E-02	23.4	2.66E-04
3.5	5.76E-02	8.5	8.84E-01	13.5	3.62E-01	18.5	1.31E-02	23.5	2.45E-04
3.6	6.65E-02	8.6	8.92E-01	13.6	3.44E-01	18.6	1.21E-02	23.6	2.26E-04
3.7	7.67E-02	8.7	8.98E-01	13.7	3.26E-01	18.7	1.13E-02	23.7	2.08E-04
3.8	8.80E-02	8.8	9.05E-01	13.8	3.09E-01	18.8	1.04E-02	23.8	1.92E-04
3.9	1.00E-01	8.9	9.11E-01	13.9	2.93E-01	18.9	9.66E-03	23.9	1.77E-04
4	1.14E-01	9	9.17E-01	14	2.77E-01	19	8.95E-03	24	1.63E-04
4.1	1.29E-01	9.1	9.22E-01	14.1	2.62E-01	19.1	8.29E-03	24.1	1.50E-04
4.2	1.45E-01	9.2	9.27E-01	14.2	2.48E-01	19.2	7.67E-03	24.2	1.38E-04
4.3	1.62E-01	9.3	9.31E-01	14.3	2.34E-01	19.3	7.10E-03	24.3	1.27E-04
4.4	1.80E-01	9.4	9.35E-01	14.4	2.21E-01	19.4	6.57E-03	24.4	1.17E-04
4.5	1.99E-01	9.5	9.39E-01	14.5	2.08E-01	19.5	6.08E-03	24.5	1.08E-04
4.6	2.18E-01	9.6	9.41E-01	14.6	1.96E-01	19.6	5.63E-03	24.6	9.91E-05
4.7	2.39E-01	9.7	9.43E-01	14.7	1.84E-01	19.7	5.20E-03	24.7	9.12E-05
4.8	2.60E-01	9.8	9.44E-01	14.8	1.74E-01	19.8	4.81E-03	24.8	8.39E-05
4.9	2.81E-01	9.9	9.45E-01	14.9	1.63E-01	19.9	4.45E-03	24.9	7.73E-05
5	3.03E-01	10	9.44E-01	15	1.53E-01	20	4.11E-03		

Input data:

Source strength = 200.2 mg DRP L<sup>-1</sup>.

Pulse duration = 6.9 PV

Partition coefficient = 1.1

Retardation factor = 6.4,

Water velocity = 3.94 cm d<sup>-1</sup>

Dispersion coefficient = 2.36 cm<sup>2</sup> d<sup>-1</sup>

**Table 3. The CXTFIT-fitted P transport data following one-dimensional convection-dispersion equation with dairy liquid.**

PV	C/C <sub>0</sub>	PV	C/C <sub>0</sub>	PV	C/C <sub>0</sub>	PV	C/C <sub>0</sub>	PV	C/C <sub>0</sub>
0	1.75E-02								
0.1	1.75E-02	5.1	1.77E-02	10.1	1.24E-01	15.1	5.18E-01	20.1	4.89E-01
0.2	1.75E-02	5.2	1.77E-02	10.2	1.30E-01	15.2	5.23E-01	20.2	4.84E-01
0.3	1.75E-02	5.3	1.77E-02	10.3	1.36E-01	15.3	5.29E-01	20.3	4.78E-01
0.4	1.75E-02	5.4	1.78E-02	10.4	1.43E-01	15.4	5.34E-01	20.4	4.72E-01
0.5	1.75E-02	5.5	1.79E-02	10.5	1.49E-01	15.5	5.39E-01	20.5	4.66E-01
0.6	1.75E-02	5.6	1.80E-02	10.6	1.56E-01	15.6	5.44E-01	20.6	4.61E-01
0.7	1.75E-02	5.7	1.81E-02	10.7	1.63E-01	15.7	5.49E-01	20.7	4.55E-01
0.8	1.75E-02	5.8	1.83E-02	10.8	1.70E-01	15.8	5.53E-01	20.8	4.49E-01
0.9	1.75E-02	5.9	1.85E-02	10.9	1.78E-01	15.9	5.57E-01	20.9	4.43E-01
1	1.75E-02	6	1.87E-02	11	1.85E-01	16	5.60E-01	21	4.37E-01
1.1	1.75E-02	6.1	1.89E-02	11.1	1.93E-01	16.1	5.64E-01	21.1	4.31E-01
1.2	1.75E-02	6.2	1.92E-02	11.2	2.00E-01	16.2	5.67E-01	21.2	4.25E-01
1.3	1.75E-02	6.3	1.96E-02	11.3	2.08E-01	16.3	5.70E-01	21.3	4.18E-01
1.4	1.75E-02	6.4	2.00E-02	11.4	2.16E-01	16.4	5.72E-01	21.4	4.12E-01
1.5	1.75E-02	6.5	2.04E-02	11.5	2.24E-01	16.5	5.74E-01	21.5	4.06E-01
1.6	1.75E-02	6.6	2.09E-02	11.6	2.32E-01	16.6	5.76E-01	21.6	4.00E-01
1.7	1.75E-02	6.7	2.15E-02	11.7	2.41E-01	16.7	5.78E-01	21.7	3.94E-01
1.8	1.75E-02	6.8	2.22E-02	11.8	2.49E-01	16.8	5.79E-01	21.8	3.88E-01
1.9	1.75E-02	6.9	2.29E-02	11.9	2.57E-01	16.9	5.80E-01	21.9	3.81E-01
2	1.75E-02	7	2.38E-02	12	2.66E-01	17	5.81E-01	22	3.75E-01
2.1	1.75E-02	7.1	2.47E-02	12.1	2.75E-01	17.1	5.82E-01	22.1	3.69E-01
2.2	1.75E-02	7.2	2.58E-02	12.2	2.83E-01	17.2	5.82E-01	22.2	3.63E-01
2.3	1.75E-02	7.3	2.69E-02	12.3	2.92E-01	17.3	5.82E-01	22.3	3.57E-01
2.4	1.75E-02	7.4	2.82E-02	12.4	3.01E-01	17.4	5.81E-01	22.4	3.51E-01
2.5	1.75E-02	7.5	2.95E-02	12.5	3.10E-01	17.5	5.81E-01	22.5	3.45E-01
2.6	1.75E-02	7.6	3.11E-02	12.6	3.19E-01	17.6	5.80E-01	22.6	3.39E-01
2.7	1.75E-02	7.7	3.27E-02	12.7	3.27E-01	17.7	5.79E-01	22.7	3.33E-01
2.8	1.75E-02	7.8	3.45E-02	12.8	3.36E-01	17.8	5.77E-01	22.8	3.27E-01
2.9	1.75E-02	7.9	3.64E-02	12.9	3.45E-01	17.9	5.76E-01	22.9	3.21E-01
3	1.75E-02	8	3.85E-02	13	3.54E-01	18	5.74E-01	23	3.15E-01
3.1	1.75E-02	8.1	4.08E-02	13.1	3.63E-01	18.1	5.72E-01	23.1	3.09E-01
3.2	1.75E-02	8.2	4.32E-02	13.2	3.72E-01	18.2	5.69E-01	23.2	3.04E-01
3.3	1.75E-02	8.3	4.58E-02	13.3	3.80E-01	18.3	5.67E-01	23.3	2.98E-01
3.4	1.75E-02	8.4	4.85E-02	13.4	3.89E-01	18.4	5.64E-01	23.4	2.92E-01
3.5	1.75E-02	8.5	5.14E-02	13.5	3.98E-01	18.5	5.61E-01	23.5	2.87E-01
3.6	1.75E-02	8.6	5.45E-02	13.6	4.06E-01	18.6	5.58E-01	23.6	2.81E-01
3.7	1.75E-02	8.7	5.78E-02	13.7	4.15E-01	18.7	5.54E-01	23.7	2.75E-01
3.8	1.75E-02	8.8	6.13E-02	13.8	4.23E-01	18.8	5.50E-01	23.8	2.70E-01
3.9	1.75E-02	8.9	6.50E-02	13.9	4.31E-01	18.9	5.47E-01	23.9	2.65E-01
4	1.75E-02	9	6.88E-02	14	4.39E-01	19	5.43E-01	24	2.59E-01
4.1	1.75E-02	9.1	7.28E-02	14.1	4.47E-01	19.1	5.38E-01	24.1	2.54E-01
4.2	1.75E-02	9.2	7.71E-02	14.2	4.55E-01	19.2	5.34E-01	24.2	2.49E-01
4.3	1.75E-02	9.3	8.15E-02	14.3	4.63E-01	19.3	5.30E-01	24.3	2.44E-01
4.4	1.75E-02	9.4	8.61E-02	14.4	4.70E-01	19.4	5.25E-01	24.4	2.39E-01
4.5	1.75E-02	9.5	9.09E-02	14.5	4.78E-01	19.5	5.20E-01	24.5	2.34E-01
4.6	1.75E-02	9.6	9.59E-02	14.6	4.85E-01	19.6	5.15E-01	24.6	2.29E-01
4.7	1.76E-02	9.7	1.01E-01	14.7	4.92E-01	19.7	5.10E-01	24.7	2.24E-01
4.8	1.76E-02	9.8	1.07E-01	14.8	4.99E-01	19.8	5.05E-01	24.8	2.19E-01
4.9	1.76E-02	9.9	1.12E-01	14.9	5.05E-01	19.9	5.00E-01	24.9	2.15E-01
5	1.76E-02	10	1.18E-01	15	5.11E-01	20	4.95E-01		

Input data:

Source strength = 23.6 mg DRP L<sup>-1</sup>.

Pulse duration = 6.9 PV

Partition coefficient = 3.1

Retardation factor = 15.4,

Water velocity = 3.94 cm d<sup>-1</sup>

Dispersion coefficient = 2.36 cm<sup>2</sup> d<sup>-1</sup>

**Table 4. The CXTFIT-fitted P transport data following one-dimensional convection-dispersion equation with swine liquid.**

PV	C/C <sub>0</sub>	PV	C/C <sub>0</sub>	PV	C/C <sub>0</sub>	PV	C/C <sub>0</sub>	PV	C/C <sub>0</sub>
0	1.75E-02								
0.1	1.75E-02	5.1	1.75E-02	10.1	5.00E-02	15.1	3.17E-01	20.1	5.03E-01
0.2	1.75E-02	5.2	1.75E-02	10.2	5.26E-02	15.2	3.24E-01	20.2	5.02E-01
0.3	1.75E-02	5.3	1.75E-02	10.3	5.52E-02	15.3	3.31E-01	20.3	5.02E-01
0.4	1.75E-02	5.4	1.75E-02	10.4	5.80E-02	15.4	3.38E-01	20.4	5.00E-01
0.5	1.75E-02	5.5	1.75E-02	10.5	6.09E-02	15.5	3.45E-01	20.5	4.99E-01
0.6	1.75E-02	5.6	1.76E-02	10.6	6.39E-02	15.6	3.51E-01	20.6	4.98E-01
0.7	1.75E-02	5.7	1.76E-02	10.7	6.71E-02	15.7	3.58E-01	20.7	4.96E-01
0.8	1.75E-02	5.8	1.76E-02	10.8	7.04E-02	15.8	3.65E-01	20.8	4.95E-01
0.9	1.75E-02	5.9	1.76E-02	10.9	7.38E-02	15.9	3.71E-01	20.9	4.93E-01
1	1.75E-02	6	1.76E-02	11	7.74E-02	16	3.77E-01	21	4.91E-01
1.1	1.75E-02	6.1	1.77E-02	11.1	8.11E-02	16.1	3.84E-01	21.1	4.89E-01
1.2	1.75E-02	6.2	1.77E-02	11.2	8.49E-02	16.2	3.90E-01	21.2	4.87E-01
1.3	1.75E-02	6.3	1.77E-02	11.3	8.89E-02	16.3	3.96E-01	21.3	4.84E-01
1.4	1.75E-02	6.4	1.78E-02	11.4	9.30E-02	16.4	4.02E-01	21.4	4.82E-01
1.5	1.75E-02	6.5	1.78E-02	11.5	9.72E-02	16.5	4.08E-01	21.5	4.79E-01
1.6	1.75E-02	6.6	1.79E-02	11.6	1.02E-01	16.6	4.13E-01	21.6	4.76E-01
1.7	1.75E-02	6.7	1.80E-02	11.7	1.06E-01	16.7	4.19E-01	21.7	4.73E-01
1.8	1.75E-02	6.8	1.81E-02	11.8	1.11E-01	16.8	4.24E-01	21.8	4.71E-01
1.9	1.75E-02	6.9	1.82E-02	11.9	1.16E-01	16.9	4.29E-01	21.9	4.67E-01
2	1.75E-02	7	1.84E-02	12	1.20E-01	17	4.35E-01	22	4.64E-01
2.1	1.75E-02	7.1	1.85E-02	12.1	1.25E-01	17.1	4.39E-01	22.1	4.61E-01
2.2	1.75E-02	7.2	1.87E-02	12.2	1.31E-01	17.2	4.44E-01	22.2	4.58E-01
2.3	1.75E-02	7.3	1.90E-02	12.3	1.36E-01	17.3	4.49E-01	22.3	4.54E-01
2.4	1.75E-02	7.4	1.92E-02	12.4	1.41E-01	17.4	4.53E-01	22.4	4.51E-01
2.5	1.75E-02	7.5	1.95E-02	12.5	1.47E-01	17.5	4.58E-01	22.5	4.47E-01
2.6	1.75E-02	7.6	1.98E-02	12.6	1.52E-01	17.6	4.62E-01	22.6	4.43E-01
2.7	1.75E-02	7.7	2.02E-02	12.7	1.58E-01	17.7	4.66E-01	22.7	4.40E-01
2.8	1.75E-02	7.8	2.06E-02	12.8	1.64E-01	17.8	4.69E-01	22.8	4.36E-01
2.9	1.75E-02	7.9	2.10E-02	12.9	1.70E-01	17.9	4.73E-01	22.9	4.32E-01
3	1.75E-02	8	2.15E-02	13	1.76E-01	18	4.76E-01	23	4.28E-01
3.1	1.75E-02	8.1	2.20E-02	13.1	1.82E-01	18.1	4.79E-01	23.1	4.24E-01
3.2	1.75E-02	8.2	2.27E-02	13.2	1.88E-01	18.2	4.82E-01	23.2	4.20E-01
3.3	1.75E-02	8.3	2.33E-02	13.3	1.95E-01	18.3	4.85E-01	23.3	4.16E-01
3.4	1.75E-02	8.4	2.41E-02	13.4	2.01E-01	18.4	4.88E-01	23.4	4.11E-01
3.5	1.75E-02	8.5	2.49E-02	13.5	2.08E-01	18.5	4.90E-01	23.5	4.07E-01
3.6	1.75E-02	8.6	2.57E-02	13.6	2.14E-01	18.6	4.93E-01	23.6	4.03E-01
3.7	1.75E-02	8.7	2.67E-02	13.7	2.21E-01	18.7	4.95E-01	23.7	3.99E-01
3.8	1.75E-02	8.8	2.77E-02	13.8	2.28E-01	18.8	4.96E-01	23.8	3.94E-01
3.9	1.75E-02	8.9	2.88E-02	13.9	2.34E-01	18.9	4.98E-01	23.9	3.90E-01
4	1.75E-02	9	3.00E-02	14	2.41E-01	19	4.99E-01	24	3.86E-01
4.1	1.75E-02	9.1	3.13E-02	14.1	2.48E-01	19.1	5.01E-01	24.1	3.81E-01
4.2	1.75E-02	9.2	3.27E-02	14.2	2.55E-01	19.2	5.02E-01	24.2	3.77E-01
4.3	1.75E-02	9.3	3.42E-02	14.3	2.62E-01	19.3	5.03E-01	24.3	3.72E-01
4.4	1.75E-02	9.4	3.58E-02	14.4	2.69E-01	19.4	5.03E-01	24.4	3.68E-01
4.5	1.75E-02	9.5	3.75E-02	14.5	2.76E-01	19.5	5.04E-01	24.5	3.63E-01
4.6	1.75E-02	9.6	3.93E-02	14.6	2.83E-01	19.6	5.04E-01	24.6	3.59E-01
4.7	1.75E-02	9.7	4.12E-02	14.7	2.90E-01	19.7	5.04E-01	24.7	3.54E-01
4.8	1.75E-02	9.8	4.32E-02	14.8	2.97E-01	19.8	5.04E-01	24.8	3.50E-01
4.9	1.75E-02	9.9	4.54E-02	14.9	3.04E-01	19.9	5.04E-01	24.9	3.45E-01
5	1.75E-02	10	4.77E-02	15	3.11E-01	20	5.04E-01		

Input data:

Source strength = 17.4 mg DRP L<sup>-1</sup>.

Pulse duration = 6.9 PV

Partition coefficient = 3.7

Retardation factor = 18.4,

Water velocity = 3.94 cm d<sup>-1</sup>

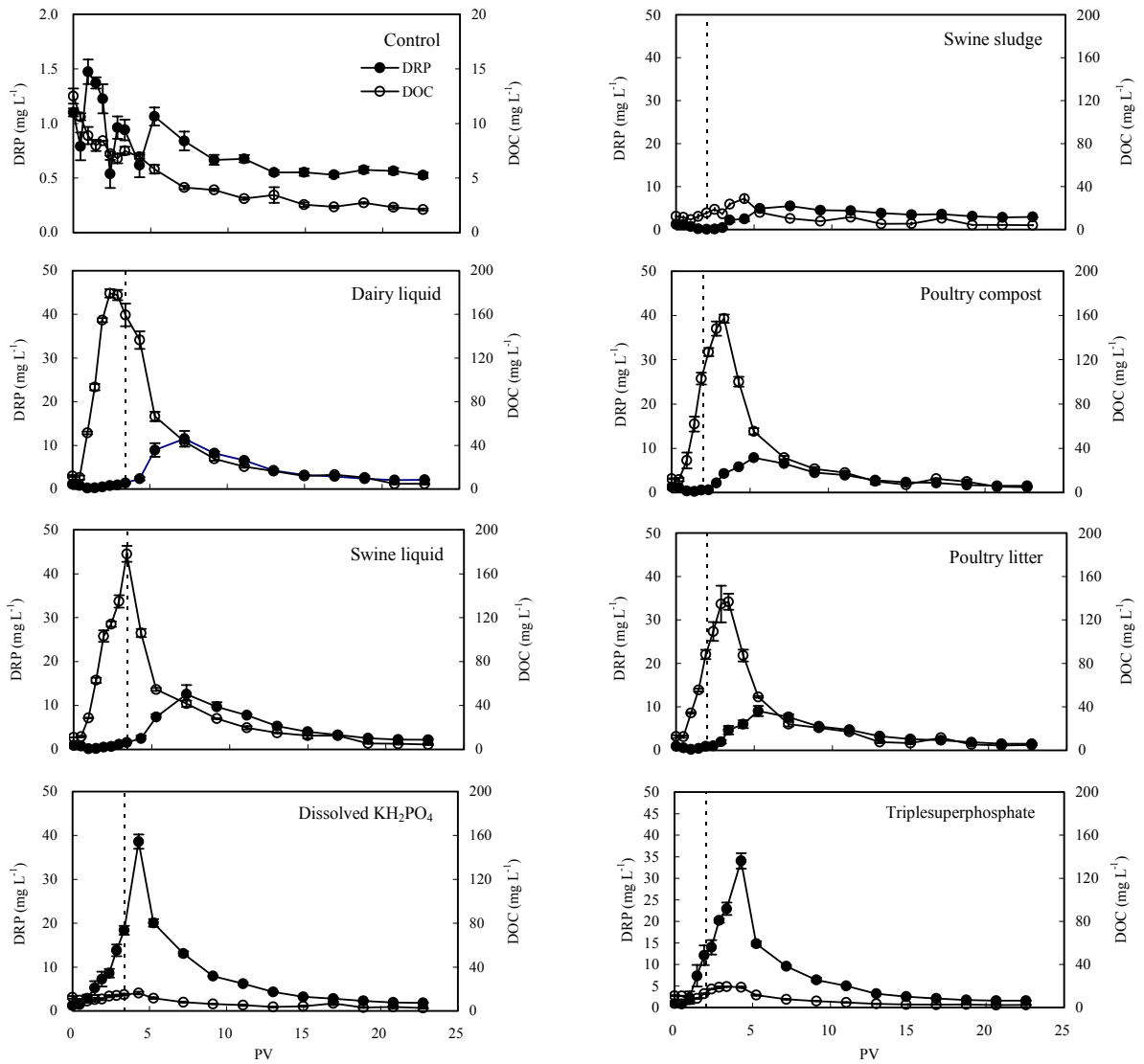
Dispersion coefficient = 2.36 cm<sup>2</sup> d<sup>-1</sup>



**Figure 1. Sand coated PVC liner and sealing to the Nalgene filter unit. From left, a clean PVC liner was coated with the study soil (coated at < 1-mm thickness) and then sealed with Nalgene filter unit for column leachate collection.**

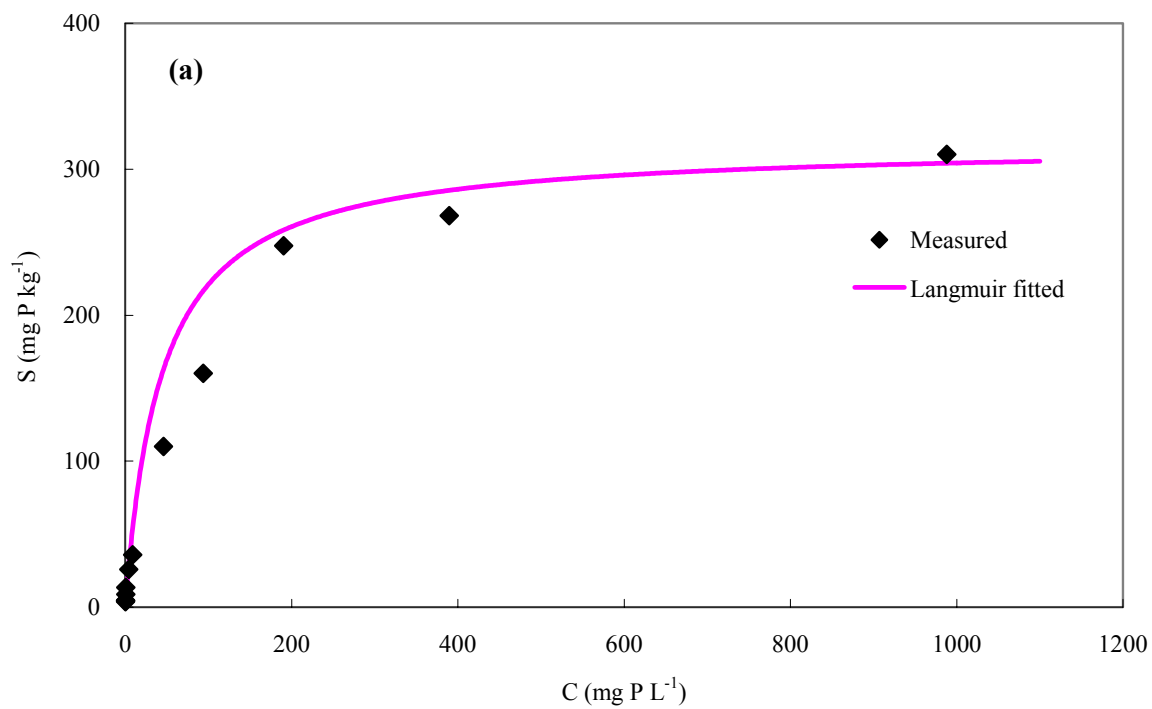


**Figure 2. Soil columns instrumented with the Nalgene funnel on the top of column and leachate bottles at the bottom of column.**

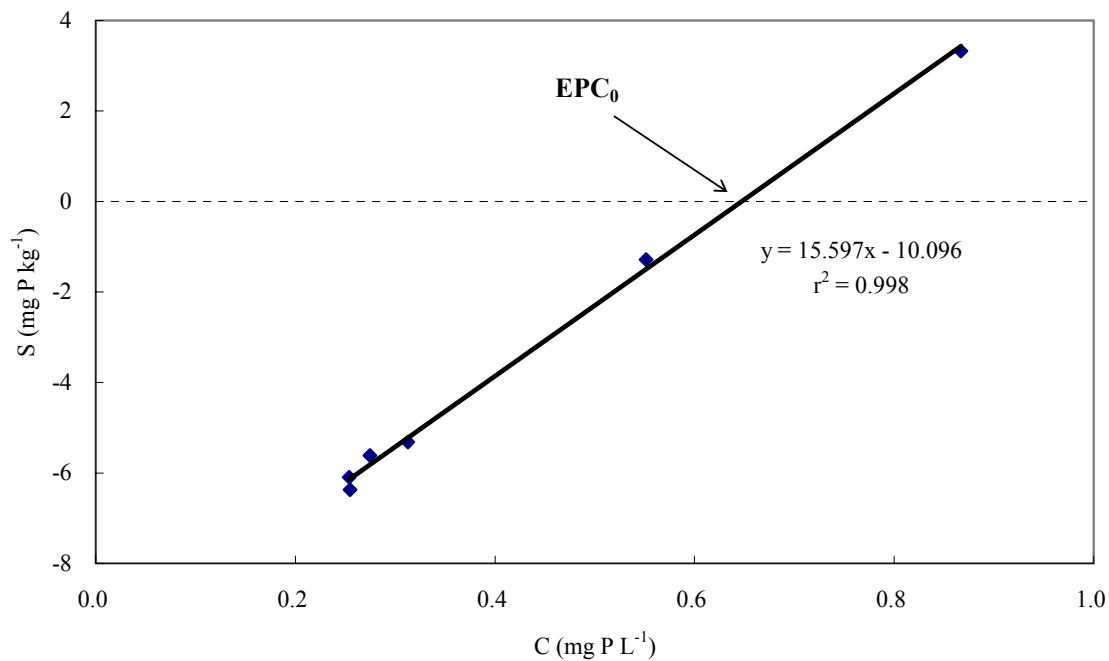


**Figure 3. Concurrent discharge of DRP and DOC in medium P load ( $75 \text{ kg P ha}^{-1}$ ). Dashed lines indicate the switching point of P source mixture to DI water. Note a different scale in control. Error bars indicates standard error of the mean volume-weighted DRP.**

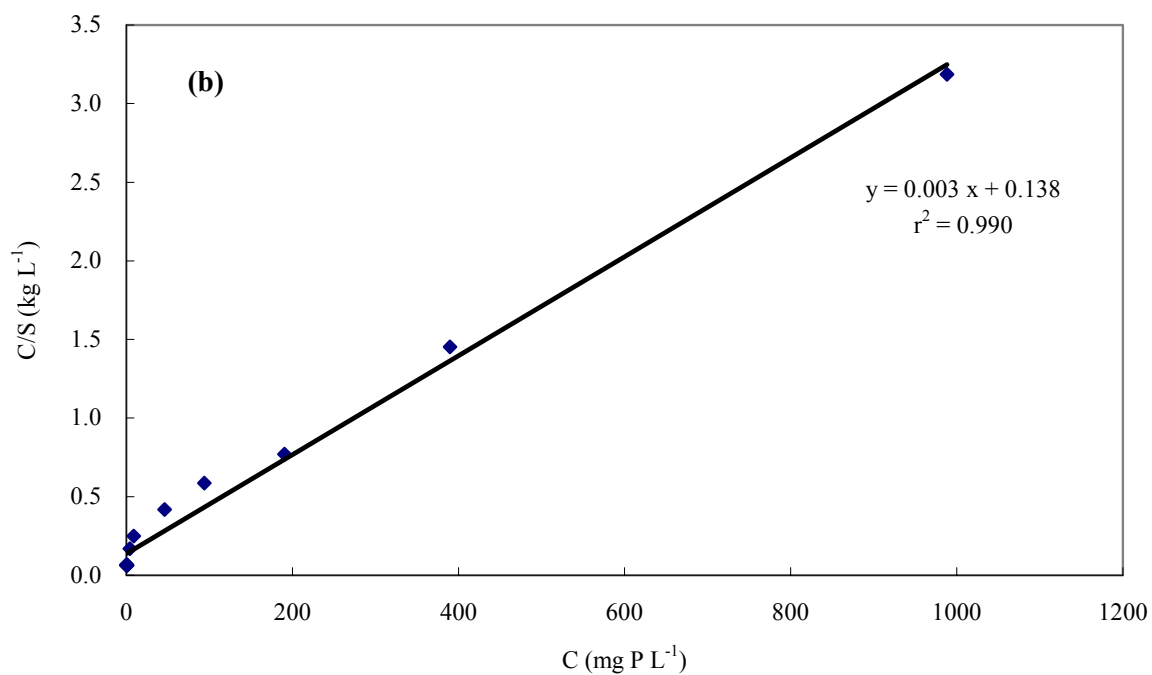




**Figure 4. P sorption isotherm to the study soil fitted with the Langmuir sorption isotherm. C is P concentration in solution (mg P L<sup>-1</sup>) and S is P sorbed (mg kg<sup>-1</sup>).**



**Figure 5. Linear portion of P sorption isotherm at the low P concentration (0 – 1 mg P L<sup>-1</sup>). C is P concentration in solution (mg P L<sup>-1</sup>) and S is P sorbed (mg kg<sup>-1</sup> soil).  $EPC_0$  is defined as the P concentration in solution where no net sorption and desorption of P occurs.**



**Figure 6. P sorption data fitted with the linearized Langmuir model**

### Appendix C. supporting materials for chapter 3

**Table 1. Raw data for phosphorus sorption.**

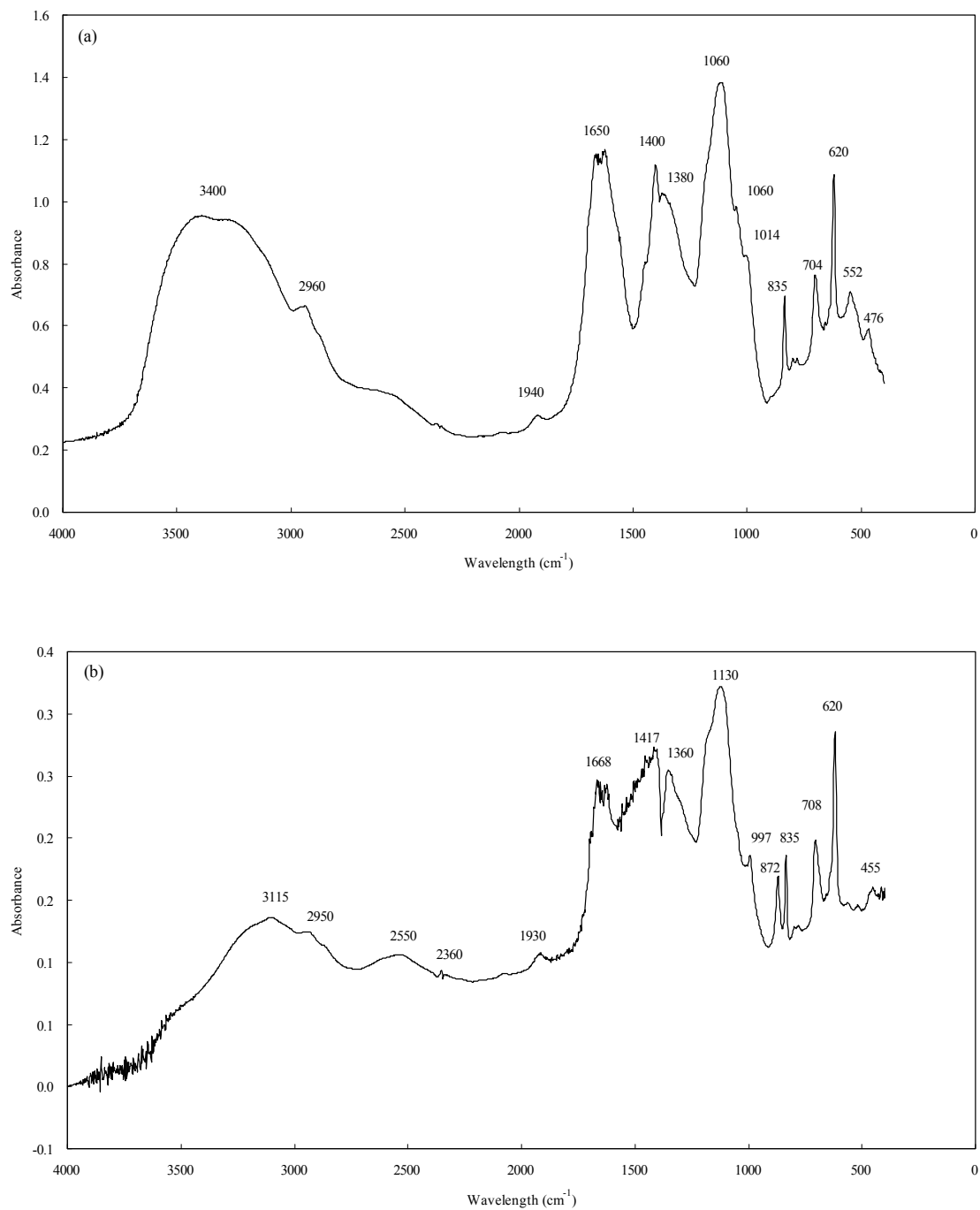
Source	Soil mass (g)	P added (mg/kg)	Vol (mL)	Initial conc (mg/L)	Final conc (mg/L)	P sorbed/desorbed (mg/kg)
KH <sub>2</sub> PO <sub>4</sub>	2.0	1492	30.0	100	93.8	92.51
KH <sub>2</sub> PO <sub>4</sub>	2.0	822	30.0	54.8	49.8	75.00
KH <sub>2</sub> PO <sub>4</sub>	2.0	330	30.0	22.2	20.4	26.73
KH <sub>2</sub> PO <sub>4</sub>	2.0	165	30.0	11.1	10.3	11.89
KH <sub>2</sub> PO <sub>4</sub>	2.0	84	30.0	5.58	5.27	4.65
KH <sub>2</sub> PO <sub>4</sub>	2.0	34	30.0	2.28	2.24	0.59
KH <sub>2</sub> PO <sub>4</sub>	2.0	17	30.0	1.12	1.4	-4.18
KH <sub>2</sub> PO <sub>4</sub>	2.0	0	30.0	0	0.99	-14.87
Poultry litter	2.0	1621	30.0	108	102	90.03
Poultry litter	2.0	826	30.0	55.6	51	68.32
Poultry litter	2.0	338	30.0	22.5	20.7	27.01
Poultry litter	2.0	171	30.0	11.5	10.1	20.79
Poultry litter	2.0	85	30.0	5.65	5.11	8.10
Poultry litter	2.0	35	30.0	2.34	2.4	-0.90
Poultry litter	2.0	14	30.0	0.95	1.32	-5.52
Poultry litter	2.0	0	30.0	0	0.99	-14.87
Swine sludge	2.0	1036	30.0	69.4	63.2	92.54
Swine sludge	2.0	528	30.0	35.2	31.8	50.98
Swine sludge	2.0	210	30.0	14.1	12.1	29.85
Swine sludge	2.0	108	30.0	7.14	6.08	15.99
Swine sludge	2.0	52	30.0	3.49	3.08	6.15
Swine sludge	2.0	16	30.0	1.03	1.44	-6.18
Swine sludge	2.0	0	30.0	0	0.99	-14.87

**Table 2. Raw data for dissolved organic carbon (DOC) sorption.**

Source	Soil mass (g)	DOC added (mg/kg)	Vol (mL)	Initial conc (mg/L)	Final conc (mg/L)	DOC sorbed/desorbed (mg/kg)
Poultry litter	2.0	9221	30.0	614.5	601.9	189.06
Poultry litter	2.0	4460	30.0	300.3	294.5	86.14
Poultry litter	2.0	1720	30.0	114.7	111.8	42.31
Poultry litter	2.0	863	30.0	58.1	59.7	-23.32
Poultry litter	2.0	424	30.0	28.3	30.9	-38.84
Poultry litter	2.0	185	30.0	12.3	16.2	-58.50
Poultry litter	2.0	92	30.0	6.2	10.9	-71.17
Swine sludge	2.0	762	30.0	51.0	48.1	44.48
Swine sludge	2.0	362	30.0	24.2	28.1	-59.53
Swine sludge	2.0	159	30.0	10.7	13.9	-47.61
Swine sludge	2.0	81	30.0	5.3	8.8	-52.72
Swine sludge	2.0	108	30.0	7.2	11.9	-69.91
Swine sludge	1.0	1516	30.0	51.0	46.5	136.34
Swine sludge	0.5	3062	30.0	51.0	46.5	270.00
Swine sludge	2.0	23	30.0	1.6	5.3	-56.97
Swine sludge	2.0	18	30.0	1.2	5.4	-63.94
Citric acid	2.0	7317	30.0	492.7	491.7	14.85
Citric acid	2.0	3699	30.0	247.9	190.0	863.89
Citric acid	2.0	1519	30.0	101.8	84.4	259.25
Citric acid	2.0	750	30.0	49.7	37.0	192.28
Citric acid	2.0	170	30.0	11.3	13.7	-37.22
Citric acid	2.0	117	30.0	7.9	10.9	-45.34

**Table 3. Summary of functional groups in the FTIR spectra of manure extracts (poultry litter and swine sludge).**

Wavenumber (cm-1)	Assignment
4300	O-H and N-H stretching from carboxylic acids, phenols and H <sub>2</sub> O
2940	Aliphatic C-H stretching
2560	O-H stretch of H-bonded COOH
1670	C=O stretching of amide groups (amide I band) and quinone and/or H-bonded conjugated ketone
1630	aromatic C=C vibration and symmetrical stretch of COO <sup>-</sup> group
1400	C-H deformation and C-O stretching of phenolic OH, COO <sup>-</sup> asymmetrical stretch
1360	Symmetric COO <sup>-</sup> stretch and/or -CH bending of aliphatics
1170-950	C-O stretching of polysaccharide-like substances
835	Aromatic C-H vibrations



**Figure 1.** The FTIR spectra of water extracts of (a) poultry litter and (b) swine sludge. Samples for FTIR spectroscopy were prepared by mixing 5 mg of the freeze-dried samples with 500 mg of pre-dried KBr, which were pressed under vacuum at 10 tons for 1-min to obtain pellets. The FTIR spectra for each extract were recorded on KBr pellets in the 4000-400 cm<sup>-1</sup> wavenumber range using an Omnic FTIR spectrophotometer (Thermo Electron Corporation, Madison, WI).

## Appendix D. Supporting materials for chapter 4.

**Table 1. Soil physical properties by depth.**

Sample ID	Soil	P source history	Depth	Texture	Clay %	Bulk density g cm <sup>-3</sup>	Particle density g cm <sup>-3</sup>	Porosity cm <sup>3</sup> cm <sup>-3</sup>	Segment Pore volume cm <sup>3</sup>	Column Pore volume cm <sup>3</sup>
ASD1	Autryville	Swine liquid	0-15	sand	1.7	1.5	2.7	0.45	223	
ASD2	Autryville	Swine liquid	15-30	sand	1.1	1.6	2.3	0.32	158	
ASD3	Autryville	Swine liquid	30-45	sand	3.4	1.6	2.7	0.40	201	
ASD4	Autryville	Swine liquid	45-60	loamy sand	7.1	1.4	2.6	0.46	228	
ASD5	Autryville	Swine liquid	60-75	sandy loam	11.2	1.3	2.7	0.50	247	
ASD6	Autryville	Swine liquid	75-90	sand	4.8	1.4	2.6	0.48	240	1298
APD1	Autryville	Poultry litter	0-15	sand	2.3	1.5	2.6	0.42	211	
APD2	Autryville	Poultry litter	15-30	loamy sand	3.4	1.5	2.5	0.41	203	
APD3	Autryville	Poultry litter	30-45	loamy sand	5.6	1.5	2.7	0.45	226	
APD4	Autryville	Poultry litter	45-60	sandy clay loam	25.5	1.1	2.5	0.54	271	
APD5	Autryville	Poultry litter	60-75	sandy clay loam	25.5	1.2	2.7	0.57	282	
APD6	Autryville	Poultry litter	75-90	sandy clay loam	25.0	1.2	2.6	0.54	270	1463
AFD1	Autryville	TSP	0-15	sand	1.4	1.5	2.7	0.44	218	
AFD2	Autryville	TSP	15-30	sand	2.8	1.5	2.6	0.42	208	
AFD3	Autryville	TSP	30-45	sand	4.0	1.6	2.7	0.41	206	
AFD4	Autryville	TSP	45-60	sand	3.0	1.5	2.7	0.44	217	
AFD5	Autryville	TSP	60-75	loamy sand	6.0	1.5	2.7	0.46	229	
AFD6	Autryville	TSP	75-90	sand	6.0	1.5	2.6	0.45	222	1299
CSD1	Cape Fear	Swine liquid	0-15	sandy loam	3.9	0.9	2.4	0.60	301	
CSD2	Cape Fear	Swine liquid	15-30	sandy loam	4.0	1.0	2.4	0.56	280	
CSD3	Cape Fear	Swine liquid	30-45	loamy sand	2.7	1.0	2.6	0.61	302	
CSD4	Cape Fear	Swine liquid	45-60	clay loam	34.9	1.1	2.6	0.59	296	
CSD5	Cape Fear	Swine liquid	60-75	clay loam	33.8	1.1	2.6	0.58	287	
CSD6	Cape Fear	Swine liquid	75-90	clay loam	34.5	1.1	2.6	0.57	285	1751
CPD1	Cape Fear	Poultry litter	0-15	sandy loam	2.8	1.1	2.4	0.52	261	
CPD2	Cape Fear	Poultry litter	15-30	sandy loam	2.8	1.1	2.3	0.53	262	
CPD3	Cape Fear	Poultry litter	30-45	sandy loam	2.7	1.2	2.6	0.54	268	
CPD4	Cape Fear	Poultry litter	45-60	sandy loam	4.0	1.1	2.5	0.55	272	
CPD5	Cape Fear	Poultry litter	60-75	clay loam	27.6	1.2	2.6	0.54	268	
CPD6	Cape Fear	Poultry litter	75-90	sandy clay loam	26.7	1.2	2.7	0.55	274	1605
CFD1	Cape Fear	TSP	0-15	sandy loam	2.8	1.1	2.4	0.55	272	
CFD2	Cape Fear	TSP	15-30	loamy sand	3.9	1.2	2.6	0.54	270	
CFD3	Cape Fear	TSP	30-45	clay loam	34.3	1.2	2.6	0.55	274	
CFD4	Cape Fear	TSP	45-60	clay	42.2	1.2	2.6	0.56	278	
CFD5	Cape Fear	TSP	60-75	clay loam	39.2	1.2	2.6	0.55	274	
CFD6	Cape Fear	TSP	75-90	clay loam	34.5	1.1	2.6	0.56	278	1646
GSD1	Goldsboro	Swine liquid	0-15	loamy sand	4.7	1.3	2.5	0.49	246	
GSD2	Goldsboro	Swine liquid	15-30	sandy loam	16.0	1.3	2.6	0.50	248	
GSD3	Goldsboro	Swine liquid	30-45	sandy loam	16.0	1.3	2.6	0.52	261	
GSD4	Goldsboro	Swine liquid	45-60	sandy loam	16.8	1.2	2.6	0.54	270	
GSD5	Goldsboro	Swine liquid	60-75	sandy loam	16.0	1.3	2.5	0.49	244	
GSD6	Goldsboro	Swine liquid	75-90	sandy clay loam	20.4	1.3	2.6	0.52	261	1530
GPD1	Goldsboro	Poultry litter	0-15	sand	2.6	1.4	2.6	0.49	243	
GPD2	Goldsboro	Poultry litter	15-30	loamy sand	5.1	1.3	2.6	0.50	250	
GPD3	Goldsboro	Poultry litter	30-45	sandy loam	19.7	1.2	2.6	0.54	270	
GPD4	Goldsboro	Poultry litter	45-60	sandy loam	19.8	1.2	2.6	0.55	272	
GPD5	Goldsboro	Poultry litter	60-75	sandy clay loam	24.3	1.2	2.6	0.55	275	
GPD6	Goldsboro	Poultry litter	75-90	sandy clay loam	22.4	1.2	2.6	0.54	271	1580
GFD1	Goldsboro	TSP	0-15	sandy loam	5.6	1.6	2.6	0.38	191	
GFD2	Goldsboro	TSP	15-30	sandy clay loam	20.4	1.6	2.6	0.40	201	
GFD3	Goldsboro	TSP	30-45	sandy clay loam	30.6	1.2	2.6	0.52	259	
GFD4	Goldsboro	TSP	45-60	clay loam	33.1	1.2	2.6	0.52	260	
GFD5	Goldsboro	TSP	60-75	clay	41.3	1.2	2.6	0.52	259	
GFD6	Goldsboro	TSP	75-90	clay loam	36.9	1.3	2.6	0.50	83	1253
WSD1	Wasda	Swine liquid	0-15	sandy loam	2.5	0.8	1.4	0.39	193	
WSD2	Wasda	Swine liquid	15-30	sandy loam	2.0	1.0	2.1	0.52	260	
WSD3	Wasda	Swine liquid	30-45	loamy sand	2.0	1.2	2.4	0.49	243	
WSD4	Wasda	Swine liquid	45-60	sandy clay loam	21.4	1.2	2.6	0.53	266	
WSD5	Wasda	Swine liquid	60-75	sandy clay loam	20.6	1.2	2.6	0.55	273	
WSD6	Wasda	Swine liquid	75-90	sandy loam	10.3	1.2	2.4	0.50	249	1484
WPD1	Wasda	Poultry litter	0-15	sandy loam	2.9	0.8	1.7	0.52	257	
WPD2	Wasda	Poultry litter	15-30	sandy loam	3.4	0.8	2.1	0.59	294	
WPD3	Wasda	Poultry litter	30-45	sandy loam	2.8	0.8	1.5	0.48	239	
WPD4	Wasda	Poultry litter	45-60	sandy loam	3.9	0.9	1.7	0.45	222	
WPD5	Wasda	Poultry litter	60-75	sandy loam	3.4	0.9	1.6	0.43	216	
WPD6	Wasda	Poultry litter	75-90	loamy sand	2.0	1.1	2.1	0.48	238	1465
WFD1	Wasda	TSP	0-15	sandy loam	3.0	0.6	1.5	0.58	288	
WFD2	Wasda	TSP	15-30	sandy loam	5.1	0.7	1.7	0.59	295	
WPD3	Wasda	TSP	30-45	loamy sand	2.8	0.9	2.1	0.58	287	
WFD4	Wasda	TSP	45-60	sand	1.4	1.1	2.4	0.54	271	
WFD5	Wasda	TSP	60-75	sandy loam	10.7	1.2	2.6	0.52	259	
WFD6	Wasda	TSP	75-90	sandy loam	11.4	1.2	2.6	0.53	262	1662

**Table 2. The SAS output to test nitrate concentration between saturated and unsaturated subsoils.**

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**Dependant variable = nitrate, predictive variable = site | drainage**

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The SAS System

The GLM Procedure

Dependent Variable: mgNL

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	6443.035171	1288.607034	23.52	<.0001
Error	17	931.560125	54.797654		
Corrected Total	22	7374.595296			

	R-Square	Coeff Var	Root MSE	mgNL Mean
	0.873680	18.71199	7.402544	39.56043

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Site	2	3787.759449	1893.879725	34.56	<.0001
Drainage	1	2135.909841	2135.909841	38.98	<.0001
Site*Drainage	2	519.365880	259.682940	4.74	0.0231

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Site	2	4341.960850	2170.980425	39.62	<.0001
Drainage	1	2274.252667	2274.252667	41.50	<.0001
Site*Drainage	2	519.365880	259.682940	4.74	0.0231

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**Table 3. The SAS output to test pore volume leached (PV).**

**Dependant variable = PV, predictive variable = soil | source**

The GLM Procedure

Dependent Variable: PV

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	11	26.17176057	2.37925096	34.47	<.0001
Error	29	2.00168333	0.06902356		
Corrected Total	40	28.17344390			
	R-Square	Coeff Var	Root MSE	PV Mean	
	0.928951	12.46287	0.262723	2.108049	
Source	DF	Type I SS	Mean Square	F Value	Pr > F
Soil	3	16.05731623	5.35243874	77.55	<.0001
Source	2	1.85256536	0.92628268	13.42	<.0001
Soil*Source	6	8.26187899	1.37697983	19.95	<.0001
Source	DF	Type III SS	Mean Square	F Value	Pr > F
Soil	3	18.52894411	6.17631470	89.48	<.0001
Source	2	1.84035209	0.92017604	13.33	<.0001
Soil*Source	6	8.26187899	1.37697983	19.95	<.0001

Duncan's Multiple Range Test for PV

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha 0.1  
 Error Degrees of Freedom 29  
 Error Mean Square 0.069024  
 Harmonic Mean of Cell Sizes 10.17995

Number of Means	2	3	4
Critical Range	.1979	.2087	.2155

Means with the same letter are not significantly different.

Duncan Grouping	Mean	N	Soil
A	2.9755	11	Autryvil
B	2.1856	9	Goldsbor
C	1.9645	11	Wasda
D	1.2420	10	Cape

**Table 3 (continued).**

---

**Dependant variable = PV, predictive variable = soil | source**

---

The SAS System

The GLM Procedure

Duncan's Multiple Range Test for PV

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

Alpha	0.05
Error Degrees of Freedom	29
Error Mean Square	0.069024
Harmonic Mean of Cell Sizes	13.60465

NOTE: Cell sizes are not equal.

Number of Means	2	3
Critical Range	.2060	.2165

Means with the same letter are not significantly different.

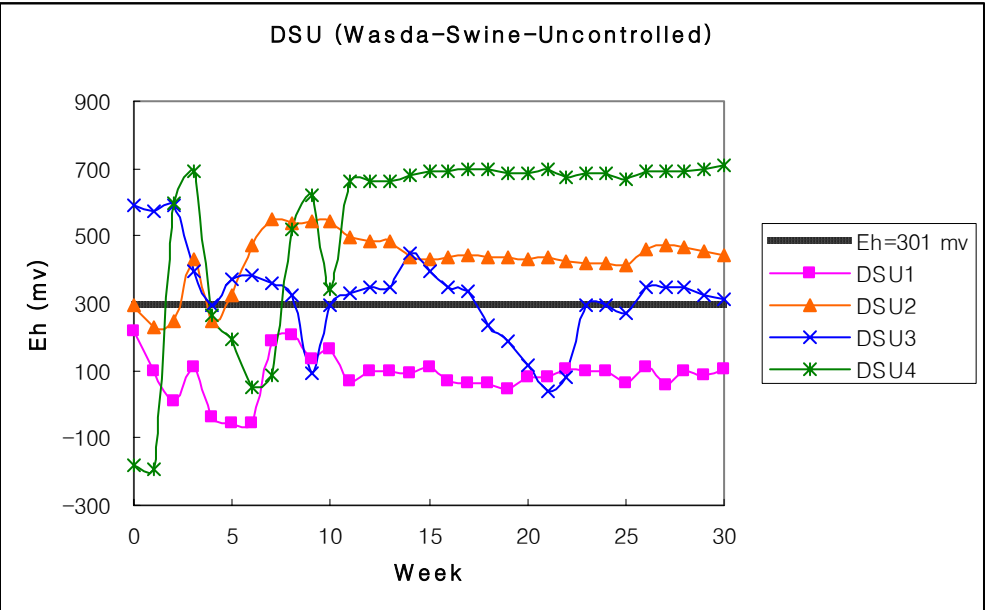
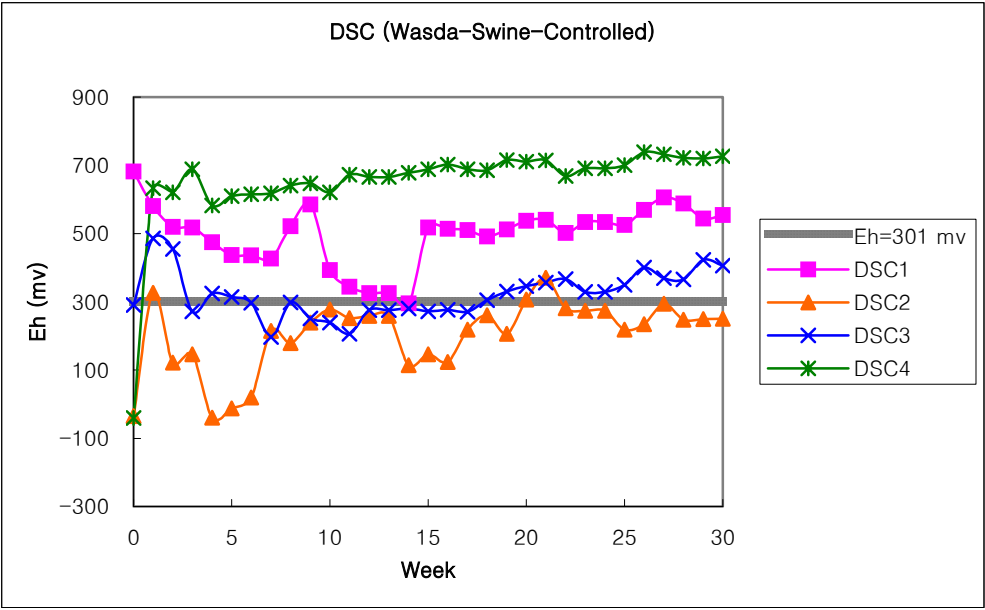
Duncan Grouping	Mean	N	Source
A	2.4069	13	Swine
B	1.9831	13	Fertiliz
B	1.9573	15	Poultry

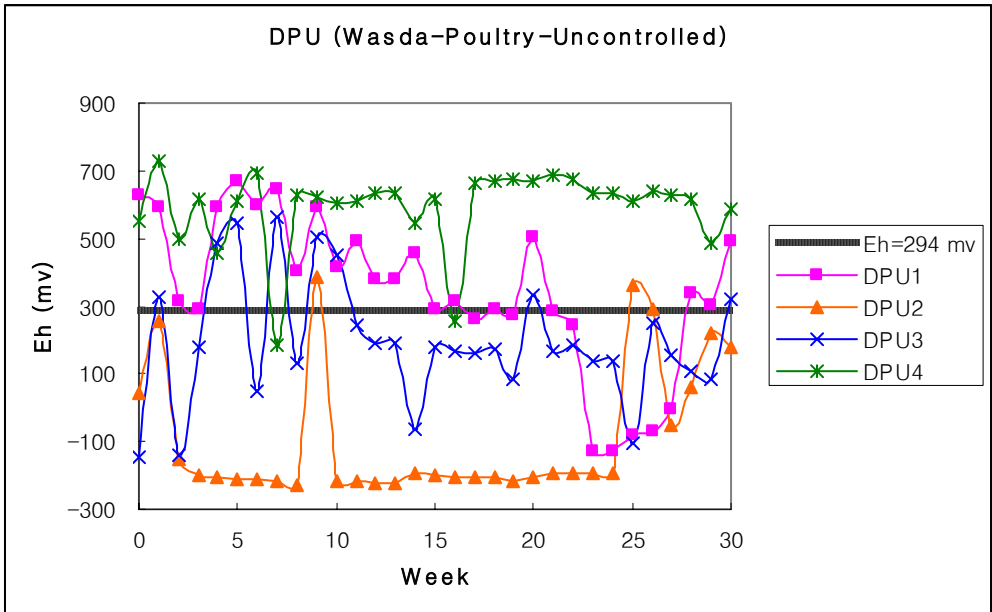
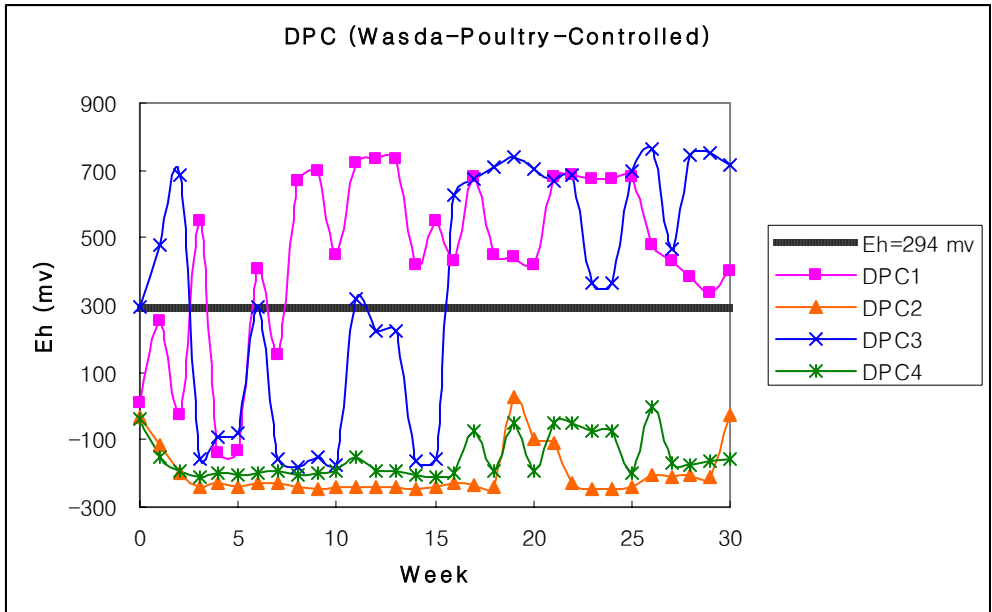
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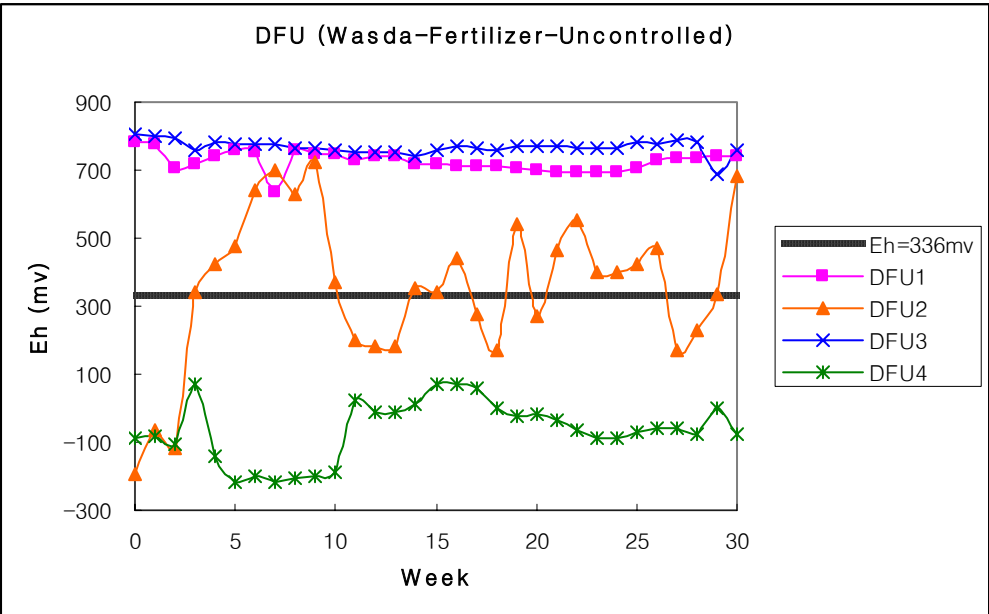
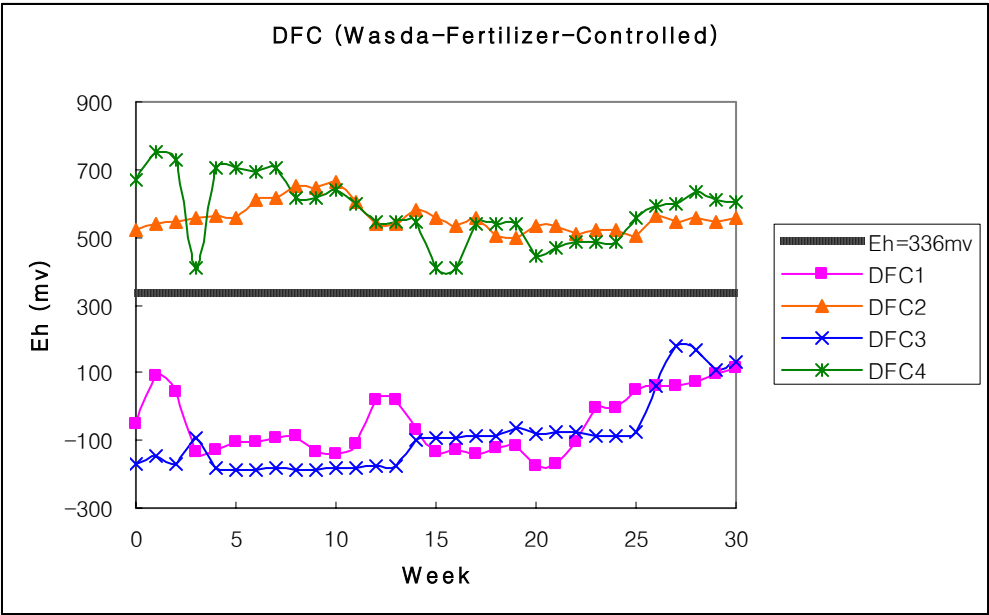
**Table 4. The SAS output to test the volume-weighted DRP concentration and mass loss of DRP.**

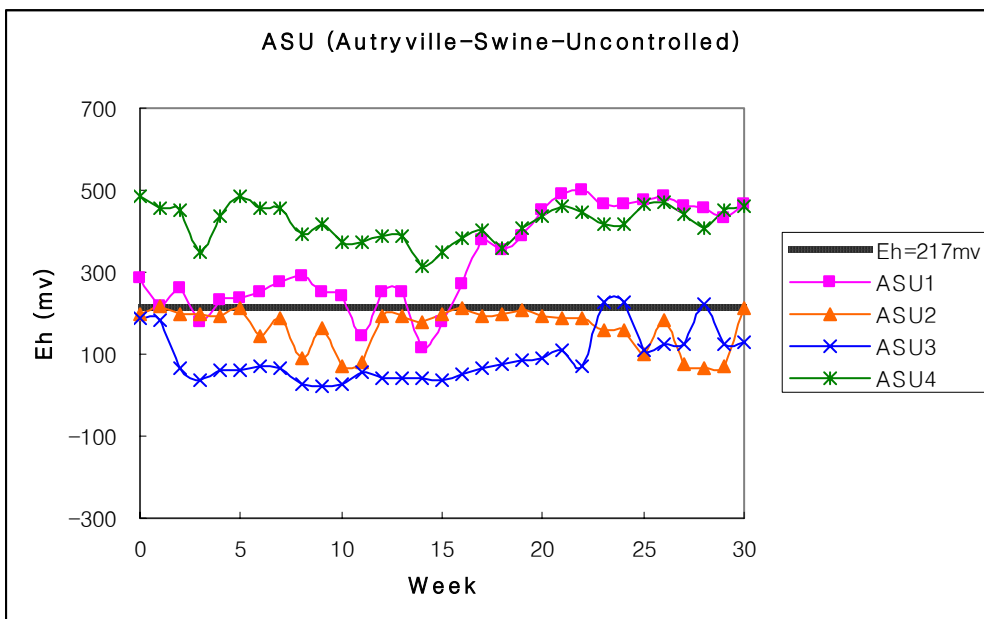
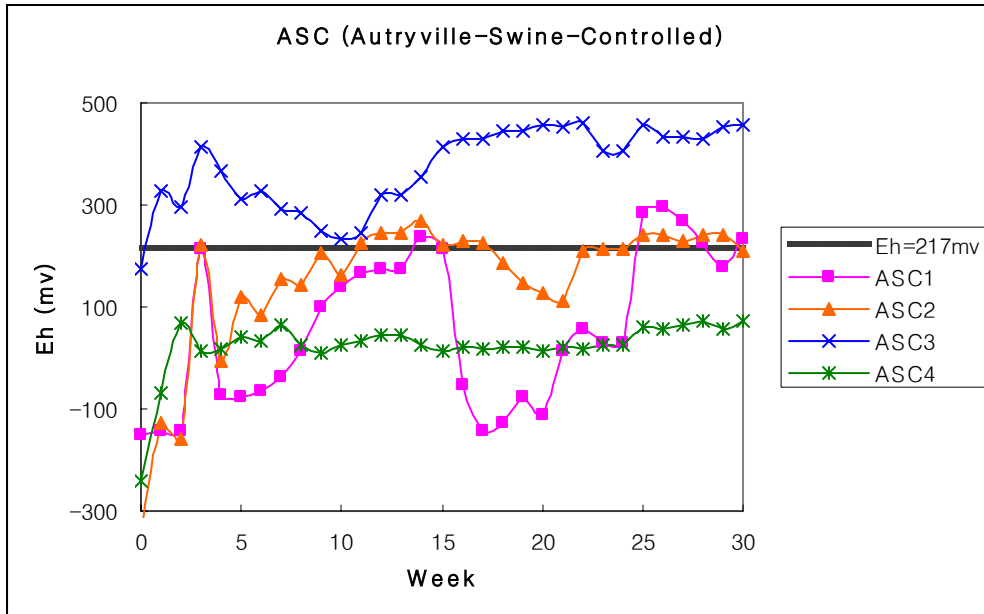
<b>Dependant variable = PV, predictive variable = soil   source</b>						
<u>Dependent Variable: mgPL (he volume-weighted DRP)</u>						
		Sum of				
Source	DF	Squares	Mean Square	F Value	Pr > F	
Model	11	0.00341931	0.00031085	4.21	0.0009	
Error	29	0.00214167	0.00007385			
Corrected Total	40	0.00556098				
	R-Square	Coeff Var	Root MSE	mgPL Mean		
	0.614876	45.17167	0.008594	0.019024		
Source	DF	Type I SS	Mean Square	F Value	Pr > F	
Soil	3	0.00323825	0.00107942	14.62	<.0001	
Source	2	0.00006704	0.00003352	0.45	0.6396	
Soil*Source	6	0.00011402	0.00001900	0.26	0.9522	
Source	DF	Type III SS	Mean Square	F Value	Pr > F	
Soil	3	0.00315996	0.00105332	14.26	<.0001	
Source	2	0.00006253	0.00003127	0.42	0.6588	
Soil*Source	6	0.00011402	0.00001900	0.26	0.9522	
<u>Dependent Variable: kgPha (mass loss of DRP)</u>						
		Sum of				
Source	DF	Squares	Mean Square	F Value	Pr > F	
Model	11	0.27775955	0.02525087	4.42	0.0006	
Error	29	0.16559167	0.00571006			
Corrected Total	40	0.44335122				
	R-Square	Coeff Var	Root MSE	kgPha Mean		
	0.626500	42.85148	0.075565	0.176341		
Source	DF	Type I SS	Mean Square	F Value	Pr > F	
Soil	3	0.22491172	0.07497057	13.13	<.0001	
Source	2	0.00326136	0.00163068	0.29	0.7537	
Soil*Source	6	0.04958646	0.00826441	1.45	0.2310	
Source	DF	Type III SS	Mean Square	F Value	Pr > F	
Soil	3	0.21262494	0.07087498	12.41	<.0001	
Source	2	0.00336293	0.00168147	0.29	0.7471	
Soil*Source	6	0.04958646	0.00826441	1.45	0.2310	

**Figure 1. Monitoring redox potential (Eh, mv) during 30 weeks period. We originally installed platinum (pt) probe at the bottom of column (10 cm up from bottom) to monitor redox potential (Eh, mv) in a weekly basis. We observed unstable reading of Eh throughout columns and periods, so that we conclude that our measured Eh were not trustworthy. The Eh values for each treatment (soil × P source) are presented as follows for reference: (note that all Eh values were adjusted based on soil pH and a thick horizontal line indicates the threshold Eh value whether or not the soil is aerobic or anaerobic).**

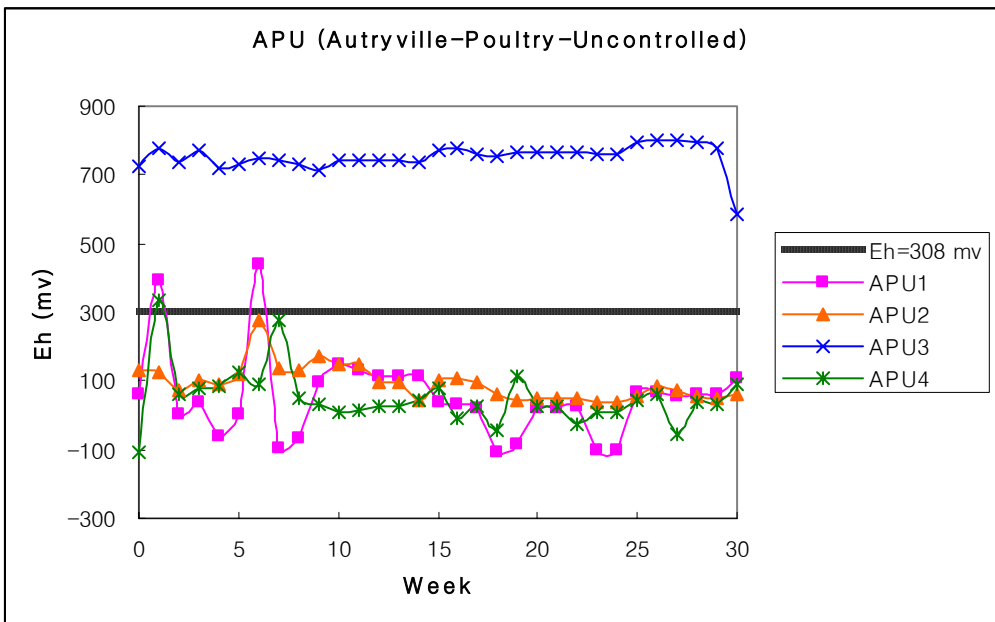
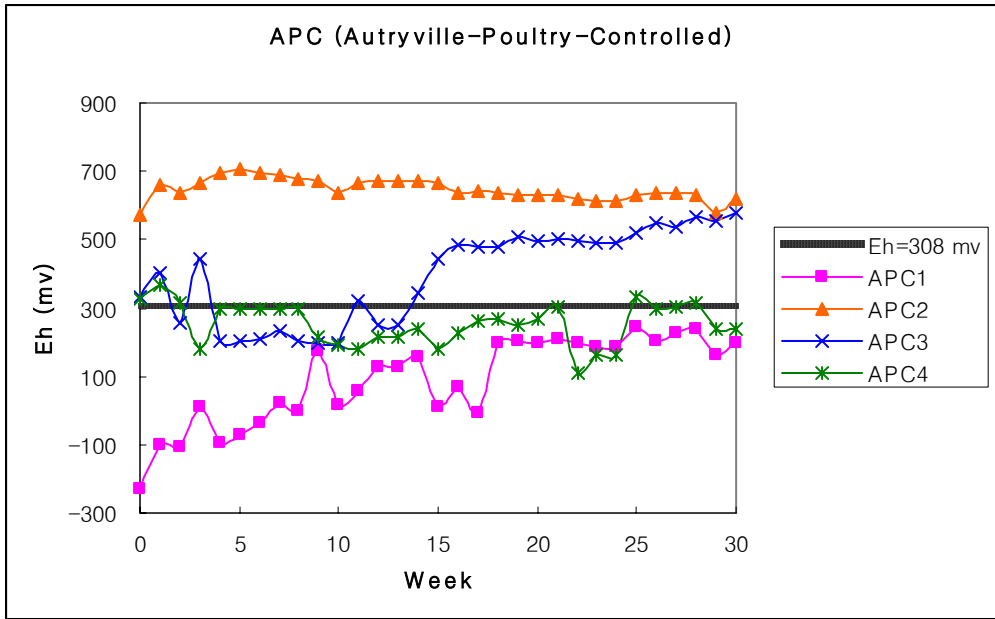


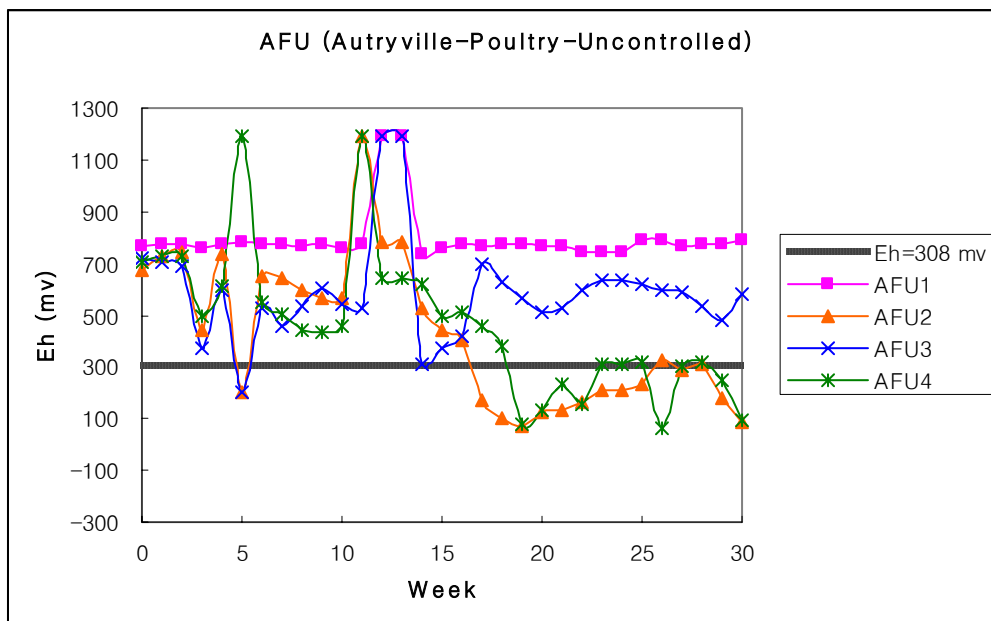
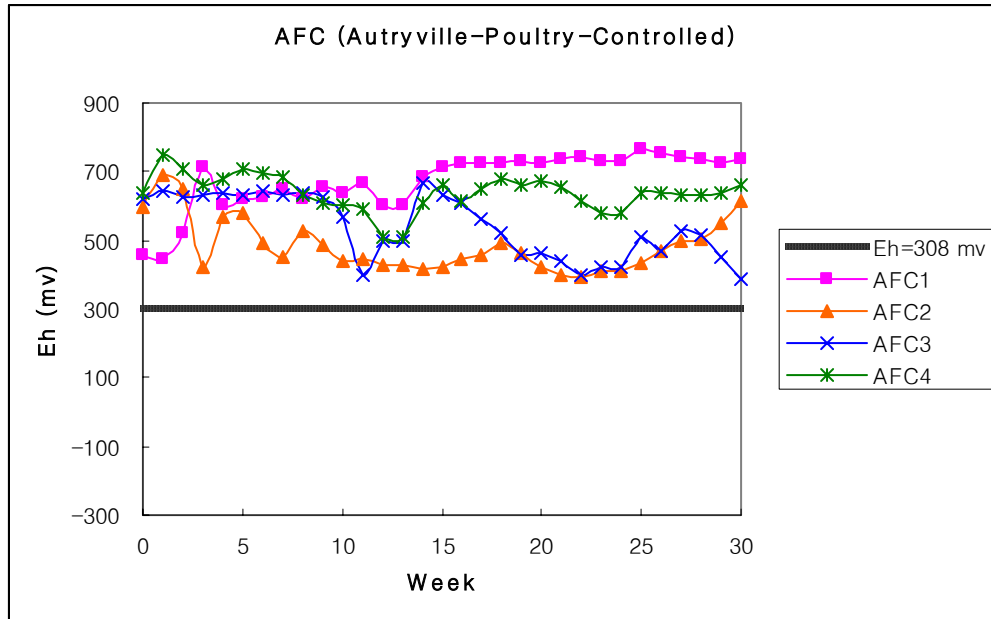


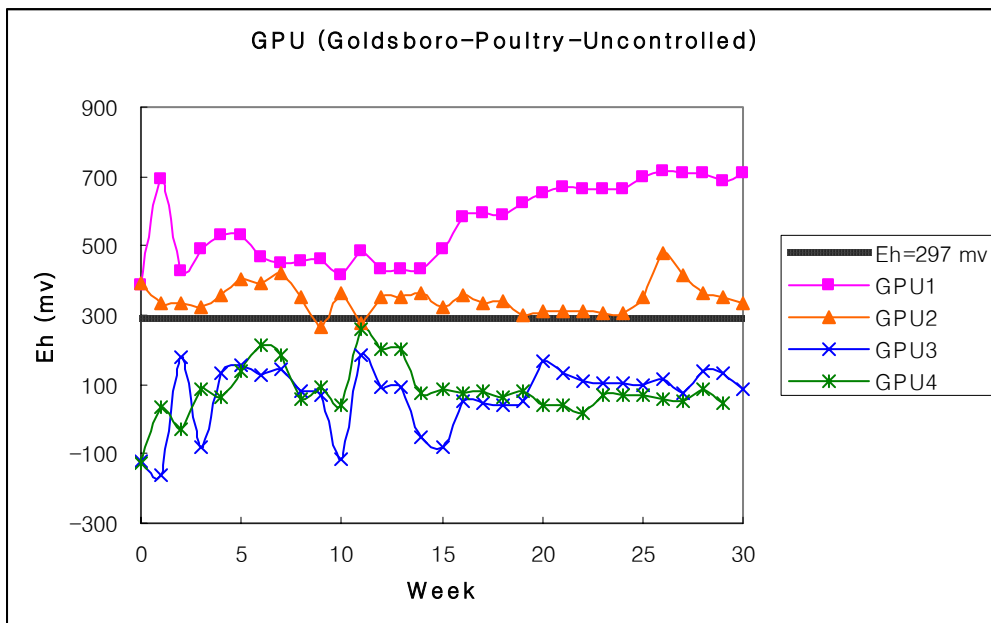
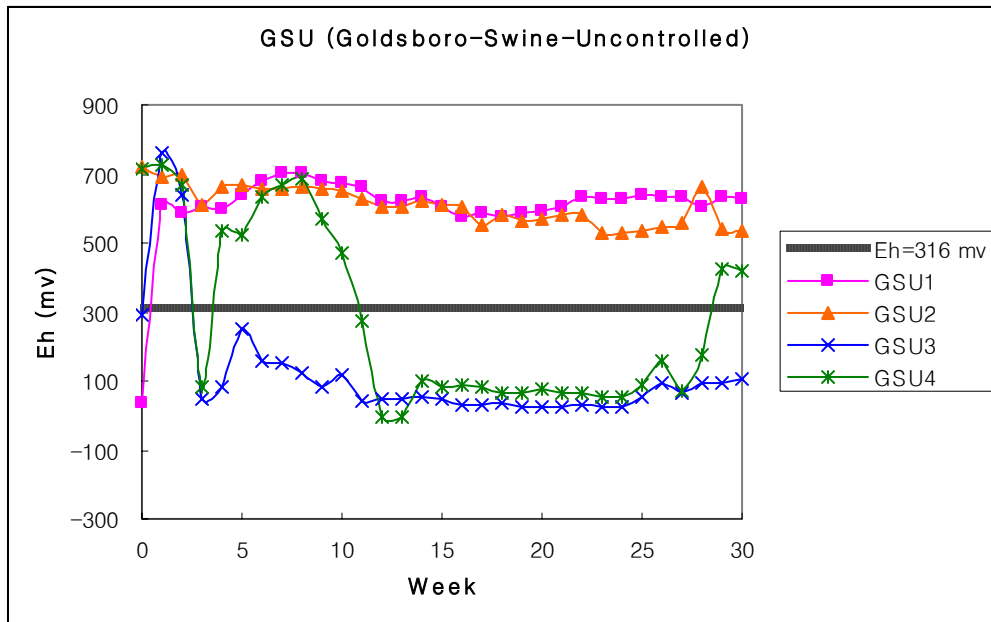


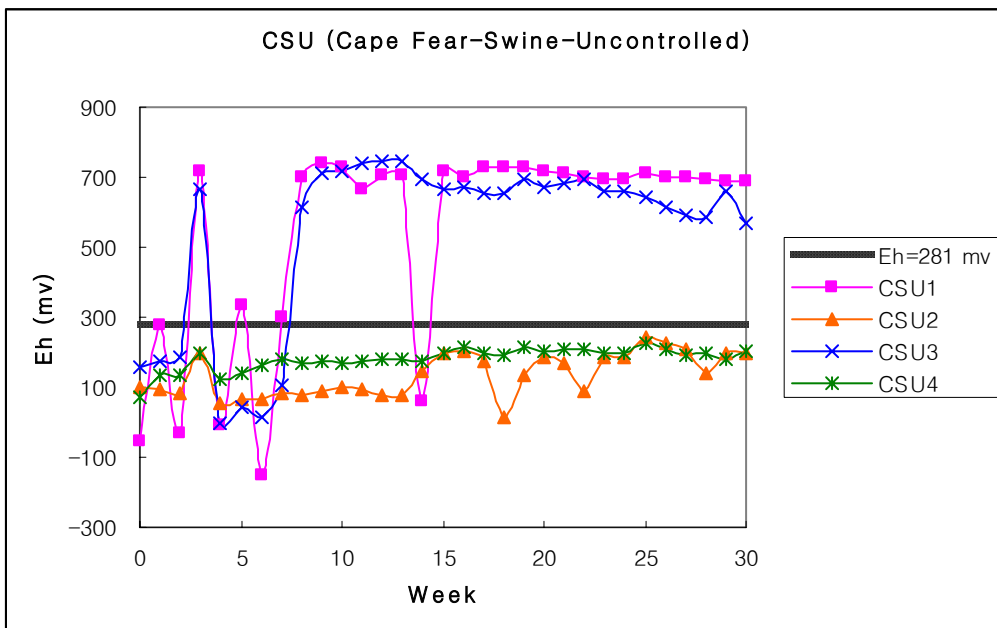
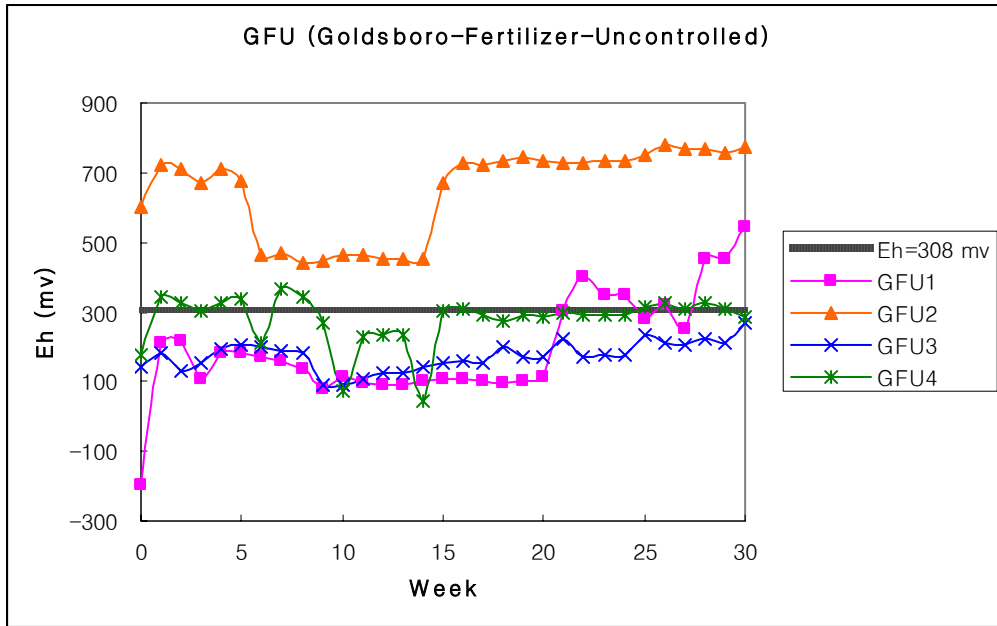


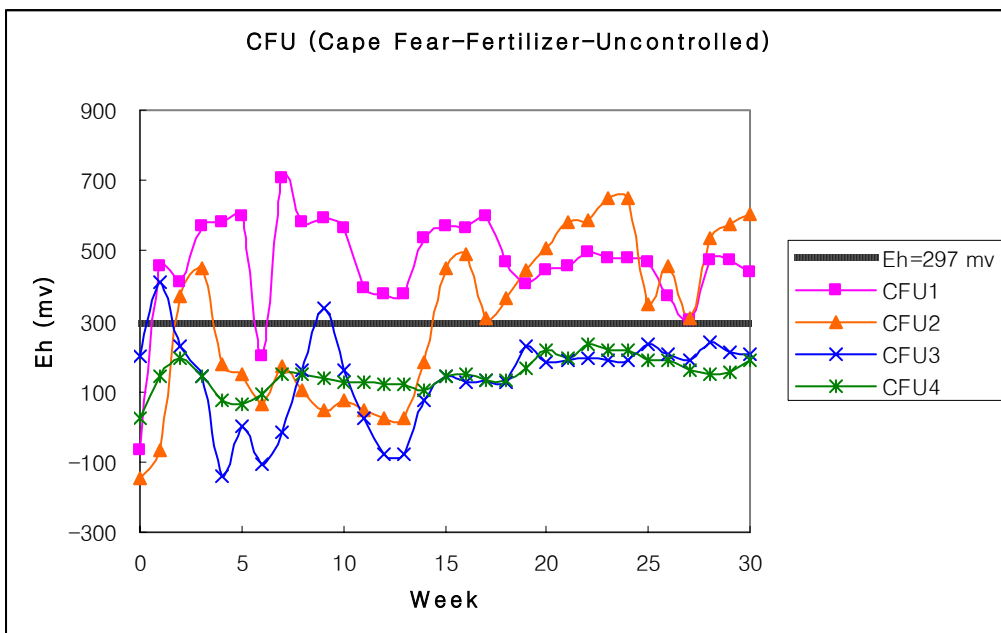
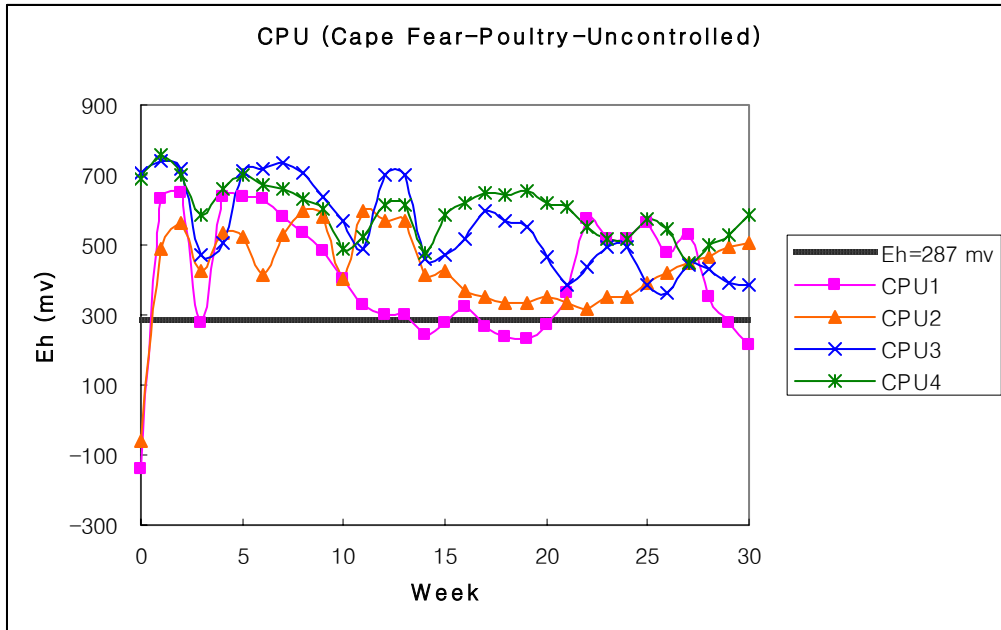












## Appendix E. Analytical protocols for soil and manure samples

### Organic matter by loss on ignition

#### **Apparatus:**

1. Pyrex beaker (50 mL)
2. High temp pen to label beaker
3. Drying oven (105 °C)
4. Muffle furnace (400 °C)
5. Analytical balance

#### **Procedures:**

1. Record weight of beaker
2. Weigh about 10 g of air-dried soil to a tared beaker.
3. Heat the beaker with soil at 105 °C for 24 h.
4. Cool the beaker and weigh soil plus beaker
5. Ignite sample in a muffle furnace at 400 °C for 16 h.
6. Cool the beaker and weigh ignited soil plus beaker
7. Calculate the soil weight at 105 °C (Weight<sub>105</sub>) and 400 °C (Weight<sub>400</sub>) by subtracting beaker weight from soil plus beaker weight.

#### **Calculations:**

Organic matter (%) =  $(\text{Weight}_{105} - \text{Weight}_{400}) / (\text{Weight}_{105}) \times 100$

#### **Reference:**

Nelson, P.W., and C.E. Sommers. 1996. Total C, organic C, and organic matter. p. 539–579. In D.L. Sparks et al. (ed.) Methods of soil analysis. Part 3. SSSA, Madison, WI.

## Water extractable phosphorus in soils

### **Apparatus:**

50-mL polyethylene centrifuge tubes  
End-over-end shaker  
Centrifuge, IEC Model K with #250 rotor  
0.45- $\mu$ m membrane  
50 mL centrifuge tubes

### **Reagents:**

DI water  
5 % H<sub>2</sub>SO<sub>4</sub> solution

### **Procedures:**

1. Weigh 3.00 g of air-dried soil sieved to pass a 2-mm sieve into a 50-mL centrifuge tube. Always include a tube with 3.00 g of standard soil to serve as a QA/QC reference.
2. Add 30 mL of deionized H<sub>2</sub>O (1:10 of soil to water ratio). Include a tube that contains only 30 mL of deionized H<sub>2</sub>O to serve as a blank.
3. Place the tubes on their side in the reciprocating shaker and shake on low speed for 1 h.
4. Centrifuge the samples at 2000 rpm (43 on the IEC centrifuge) for 13 min.
5. Using the Millipore filtration apparatus and 0.45- $\mu$ m filters, filter the supernatant from the tubes into a 40-mL tube
6. Analyze for P colorimetrically using using the Lachat QuickChem 8000 (Milwaukee, WI).. If samples are not analyzed right away, they should be refrigerated. If samples are not going to be analyzed within 24 h, they should be acidified to pH 2.0 with drops of 5 % H<sub>2</sub>SO<sub>4</sub> solution to prevent precipitation of phosphate compounds.

### **Calculations:**

Water extractable P (mg P/kg soil) =  
[Concentration of P in extract, mg/L]  $\times$  [Volume of extract, L] / [Mass of soil, kg]

### **Reference:**

Wolf, A.M., P.J.A. Kleinman, A.N. Sharpley, and D.B. Beegle. 2005. Development of a water extractable phosphorus test for manure: Inter-laboratory study. Soil Sci. Soc. Am. J. 69:695–700.

## Ammonium oxalate-extractable Al, Fe and P in soils

### **Apparatus:**

50-mL centrifuge tubes  
End-over-end shaker  
Aluminum foil  
Large cardboard box  
Centrifuge, IEC model K with #250 rotor  
Funnels  
Whatman #42 filter paper  
40-mL sample bottles

### **Reagents:**

#### *1. 0.2 M ammonium oxalate/oxalic acid extracting solution*

Dissolve 28.42 g of ammonium oxalate [(NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O, F.W.=142.11] in a 1-L volumetric flask containing approximately 800 mL of deionized H<sub>2</sub>O; bring to 1-L volume. Dissolve 25.21 g of oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, F.W.=126.06) in a second 1-L volumetric flask containing approximately 800 mL of deionized H<sub>2</sub>O; bring to 1-L volume. In a large beaker, thoroughly mix 700 mL of the 0.2 M ammonium oxalate with 535 mL of the 0.2 M oxalic acid. Check the pH of this solution. If the pH is not 3.00 ± 0.5, adjust as necessary using either the 0.2 M oxalic acid (to lower the pH) or the 0.2 M ammonium oxalate (to raise the pH). If you need to store the final solution, do so in the dark.

### **Procedure:**

1. Weigh 0.8 g of air-dried soil sieved to pass a 2-mm sieve into a 50-mL centrifuge tube.
2. Add 32 mL of the ammonium oxalate extracting solution to the tube (only add to 8 tubes at a time, as only 8 tubes can be centrifuged at one time). Wrap each tube completely in aluminum foil to keep in darkness during extraction.
3. Place 8 tubes horizontally on the reciprocating shaker and shake at low speed in darkness for 2 h at room temperature. To keep in darkness, cover the shaker with a large cardboard box. Always include a tube that contains only 40 mL of the ammonium oxalate extracting solution to serve as a blank.
4. Centrifuge at 2000 rpm (43 on the IEC centrifuge) for 13 min.
5. Using Whatman #42 filter paper, filter the supernatant from the tubes into 40-mL sample bottles.
6. Analyze by ICP.



**Reference:**

Iyengar, S.S., L.W. Zelazny, and D.C. Martens. 1981. Effect of photolytic oxalate treatments on soil hydroxyl interlayered vermiculites. *Clays Clay Miner.* 29:429-434.

McKeague, J. and J.H. Day. 1966. Dithionite and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Can. J. Soil Sci.* 46:13-22.

Pote, D.H., T.C. Daniel, A.N. Sharpley, P.A. Moore, Jr., D.R. Edwards, and D.J. Nichols. 1996. Relating extractable soil phosphorus to phosphorus losses in runoff. *Soil Sci. Soc. Am. J.* 60:855-859.

## Phosphorus sorption isotherm

### Apparatus:

50-mL centrifuge tubes  
End-over-end shaker  
Centrifuge, IEC model K with #250 rotor  
Filter apparatus (0.45- $\mu\text{m}$  membrane)  
pH meter

### Reagents:

Electrolyte: 0.01 M KCl  
Inorganic P solutions: 0, 1, 10, 25, 50, 100 and 250 mg P L<sup>-1</sup>

### Procedure:

1. Weigh 1 g of air-dried soil into a 50-mL centrifuge tube.
2. Add equivalent amount of P solution for proposed inorganic P concentrations to produce a soil:solution ratio of 1:25 (adjust pH at 6.0).
3. Place centrifuge tubes on end-to-end shaker for 24-h.
4. Filter supernatants through 0.45- $\mu\text{m}$  membrane
5. Centrifuge at 2000 rpm (43 on the IEC centrifuge) for 13 min
6. Analyze for P colorimetrically using using the Lachat QuickChem 8000 (Milwaukee, WI).

### Calculations

Phosphorus adsorbed by a soil will be calculated as follows:

$$[(C_0 \times V) - (C_t \times V)]/M = S' \quad [1]$$

where

$C_0$  = concentration of P added, mg L<sup>-1</sup>

$V$  = volume of liquid, L

$C_t$  = concentration of P in solution after 24-h equilibration, mg L<sup>-1</sup>

$M$  = mass of dry soil, kg

$S'$  = P retained by solid phase

Since equation [1] do not account for previously adsorbed P (native P), it was used to calculate the P lost (adsorbed) or released (desorbed), in relation to P during 24-h

equilibration time. The total amount (initial + added) of P sorbed by a soil will be calculated as follows:

$$S = S' + S_0 \quad [2]$$

where

$S$  = the total amount of P retained,  $\text{mg kg}^{-1}$

$S'$  = amount of added P sorbed,  $\text{mg kg}^{-1}$

$S_0$  = initially sorbed P (initial soil P present in adsorbed phase),  $\text{mg kg}^{-1}\text{g}$

The  $P_{\text{ox}}$  will be used for the calculation of  $S_0$  because it represents the P originally sorbed by amorphous Fe and Al oxides and hydroxides in acid soils (Yuan and Lavkulich, 1994; Freese et al., 1992).

Adsorption parameters will be calculated using the linearized Langmuir adsorption equation:

$$\frac{C}{S} = \frac{1}{kS_{\text{max}}} + \frac{C}{S_{\text{max}}} \quad [3]$$

$S_{\text{max}}$  = P adsorption maximum,  $\text{mg kg}^{-1}$ , and

$k$  = a constant related to the bonding energy,  $\text{L mg}^{-1}$ .

Plotting  $C/S$  on the y-axis versus  $C$  on the x-axis will give a straight line with a slope of  $(1/S_{\text{max}})$  and an intercept of  $(1/kS_{\text{max}})$ . Using linear regression, values for  $k$  and  $S_{\text{max}}$  will be obtained from the slope and intercept values. Sorption data and soil properties will be converted to mmol basis instead of mg basis for further calculation.

### **Reference:**

Freese, D., S.E.A.T.M. van der Zee, and W.H. van Riemsdijk. 1992. Comparison of different models for phosphate sorption as a function of the iron and aluminum oxides of soils. *J. Soil Sci.* 43:729-738.

Graetz, D.A., and V. D. Nair. 2000. Phosphorus sorption isotherm determination. p. 35–38. *In* G.M. Pierzynski (ed.) *Methods of phosphorus analysis for soils, sediments, residuals, and waters*. Bull. No. 369. Southern Extension Research Activity-Information Exchange (SERA-IEG-17), Kansas State University, Manhattan, KS.

Yuan, G, and L.M. Lavkulich. 1994. Phosphate sorption in relation to extractable iron and aluminum in Spodosols. *Soil Sci. Soc. Am. J.* 58:343-346.

## Water-extractable phosphorus in animal manures

### Apparatus:

1. End-over-end shaker
2. Centrifuge for a 250 mL centrifuge tube
3. Centrifuge tubes (250 mL)
4. Filtration apparatus (0.45- $\mu$ m membrane)

### Reagents:

1. DI water
2. 5 % H<sub>2</sub>SO<sub>4</sub> solution

### Procedure:

1. Weigh 1 g of dry equivalent weight of manure into a 250 mL centrifuge tube.
2. Add 100 mL of distilled water and shake for 1-h.
3. Shake the bottle for an hour in end-over-end shaker and centrifuge 10 min at 10,000 rpm.
4. Decant supernatant and filter through 0.45- $\mu$ m membrane
5. Acidify to pH 2.0 with 5 % H<sub>2</sub>SO<sub>4</sub> solution
6. Analyze for P by ICP.

### Calculations:

On a dry weight basis (mg P/kg dry manure)

Manure P (mg/kg) = [P in extract (mg/L)] x [Extractant volume (L)  $\div$  Mass of dry manure (kg)]

On a wet weight basis (mg P/kg wet manure)

Manure P conc. (wet basis) (mg/kg) = [P conc. in extract (mg/L)] x [Extractant volume (L)  $\div$  Mass of wet manure (kg)]

### References:

Self-Davis, M.L. and P.A. Moore, 2000. Determining water-soluble P in animal manure. p. 74-76. *In* G.M. Pierzynski (ed.) Methods of phosphorus analysis for soils, sediments, residuals, and waters. Bull. No. 369. Southern Extension Research Activity-Information Exchange (SERA-IEG-17), Kansas State University, Manhattan, KS.

## Dry matter analysis in animal manures

### **Apparatus:**

Drying vessels

Drying ovens (110 °C)

Analytical balance (capable of at least 0.01 g resolution)

Desiccator

*\* Thoroughly mix and homogenize the entire sample before subsampling. Minimize contact time with the open air to avoid the moisture loss from evaporation before taking the wet sample weight.*

### **Procedures:**

1. Record empty weight of drying vessel to nearest 0.01 g.
2. Add 10 g of manures and record weight of container plus wet sample to nearest 0.01 g.
3. Dry sample in over for **16-h at 110 °C**
4. Remove sample from drying oven and allow to be cooled in a desiccator with active desiccant.
5. Record weight of container plus dried sample to nearest 0.01 g.

### **Calculations:**

$$\% \text{ Dry matter} = \frac{[(\text{weight dry sample} + \text{container}) - (\text{weight empty container})] \times 100}{[(\text{weight undried sample} + \text{container}) - (\text{weight empty container})]}$$

### **Reference:**

Peters, J., S. Combs, B. Hoskins, J. Jarman, J. Kovar, M. Watson, A. Wolf, and N. Wolf. 2003. Recommended methods of manure analysis (A3769). University of Wisconsin Extension, Cooperative Extension Publishing, Madison, WI.

## Total acidity and carboxylic groups in animal manures

### 1) Total acidity

#### Reagents:

1. CO<sub>2</sub>-free DI water
2. 0.2 N Barium hydroxide [Ba(OH)<sub>2</sub>] (FW = 171.342): Dissolved 6.31 g of Barium hydroxide octahydrate [Ba(OH)<sub>2</sub>·8H<sub>2</sub>O] (FW = 315.46) into a 200-mL volumetric flask and bring this up to 200 mL. Use CO<sub>2</sub>-free DI water and protect the solution from CO<sub>2</sub> using N<sub>2</sub> gas.
3. 0.5 N HCl solution
4. Burette
5. 40 mL centrifuge tube

#### Procedures:

1. Weigh 100 mg (0.1 gram) of humic material in a 40-mL centrifuge tube.
2. Add 20 mL of 0.2 N Ba(OH)<sub>2</sub> solution.
3. Set up a blank consisting of the flask consisting of 20 mL of 0.2 N Ba(OH)<sub>2</sub> solution without humic materials.
4. Displace the air in each flask by N<sub>2</sub> gas and close the cap carefully
5. Shake for 24-h at room temperature.
6. Centrifuge at a 2500 × g for 20 min.
7. Record tare-weight of (50-mL beaker + magnetic bar).
8. Transfer the supernatant into a 50-mL beaker
9. Record the weight of supernatant
10. Adjust the volume of blank close to that of supernatant
11. Titrate the filtrate plus washing potentiometrically with standard 0.5 N HCl solution to pH 8.4. This should be done under N<sub>2</sub> gas.
12. Record titrated volume of 0.5 N HCl solution.

#### Calculations:

$$\text{Total acidity} = \frac{(\text{Titer for blank} - \text{Titer for sample}) \times \text{Normality acid} \times 1000}{\text{Weight of sample (mg)}}$$

Total acidity = meq total acidity / g of humic material

Titer for blank (mL) = volume of 0.5 N HCl solution used with the blank for the titration

to pH 8.4.

Titer for sample (mL) = volume of 0.5 N HCl solution used with the (filtrate + washing) for the titration to pH 8.4.

## 2) Carboxylate group (COOH) groups

### Reagents:

CO<sub>2</sub>-free DI water

1 N calcium acetate [(CH<sub>3</sub>COO)<sub>2</sub>Ca· H<sub>2</sub>O; Ca(OAc)<sub>2</sub>]

0.1 N NaOH

### Procedure:

1. Weigh 100mg (=0.1 gram) of humic material in a 125-mL ground-glass stoppered Erlenmeyer flask.
2. Add 10 mL of 1 N Ca(OAc)<sub>2</sub> solution and 40 mL of DI water.
3. Set up a blank consisting of the flask consisting of 10 mL of 1 N Ca(OAc)<sub>2</sub> solution and 40 mL of DI water without humic materials.
4. Displace the air in each flask by N<sub>2</sub> and stopper the flask carefully
5. Shake for 24-h at room temperature.
6. Prepared another 125-mL ground-glass stoppered Erlenmeyer flask for storing filtrate.
7. Record tare-weight of (empty flask + magnetic bar).
8. Filter the suspension to the prepared flask.
9. Wash the residue thoroughly with DI water
10. Weigh (filtered samples + the washing), which should be close to 50 mL.
11. Titrate the filtrate plus washing potentiometrically with standard 0.1 N NaOH solution to pH 9.8.

### Calculations:

$$\text{COOH groups} = \frac{(\text{Titer for blank} - \text{Titer for sample}) \times \text{Normality base} \times 1000}{\text{Weight of sample (mg)}}$$

COOH groups = meq COOH / g of humic material

Titer for blank (mL) = volume of 0.1 N NaOH solution used with the blank for the titration to pH 9.8.

Titer for sample (mL) = volume of 0.1 N NaOH solution used with the (filtrate + washing) for the titration to pH 9.8.

**Phenolic OH groups (meq phenolic OH / g of humic material)**

**= (meq total acidity / g of humic material) – (meq COOH / g of humic material)**

**Reference:**

Schnitzer, M. 1982. Organic matter characterization. In Methods of Soil analysis, 2nd ed.; Agronomy Monograph p; Page et al., eds.; ASA-SSSA: Madison, WI. pp. 581-594.