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PHOSPHORUS SORPTION AND AVAILABILITY FROM
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presented by

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of the requirements for the

M.S. degree in Crop and Soil Sciences

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**PHOSPHORUS SORPTION AND AVAILABILITY FROM MANURES FOR
SELECTED MICHIGAN SOILS**

By

Sarah Kathleen Marshall

A THESIS

**Submitted to
Michigan State University
in partial fulfillment of the requirements
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ABSTRACT

PHOSPHORUS SORPTION AND AVAILABILITY FROM MANURES FOR SELECTED MICHIGAN SOILS

By

Sarah Kathleen Marshall

A method was developed to determine if inorganic P (P_i) and total P (P_t) sorption to soil was different when potassium phosphate (KH_2PO_4), dairy slurry, or swine slurry was used as the P source. Sorption isotherms were constructed and compared. P_i sorption capacities for all soils decreased in the following order: dairy slurry > KH_2PO_4 \geq swine slurry. Overall, P_i sorption strength of either manure slurry was less than KH_2PO_4 . For all soils, P_i sorption capacity for either manure slurry was greater than KH_2PO_4 and sorption strength for dairy and swine slurries was reduced or unchanged. Desorption of Fe and Al from soil occurred when dairy and swine slurries were used as the P source; however, no apparent desorption occurred for KH_2PO_4 solutions, this may be caused by organic acids in the manure solutions. The difference in P_i sorption between dairy slurry and KH_2PO_4 was moderately correlated to desorbed Fe and Al for five soils however, this correlation did not exist for swine slurry and KH_2PO_4 . In an incubation experiment, soil was amended with dairy slurry, swine slurry, or fertilizer. Overall, incubation with any amendment reduced sorption capacity and strength for at least three soils. Relative P availability from the different P sources increased as follows: dairy < swine \leq fertilizer. The results from these studies suggest that P sorption characteristics depend on the P source and P availability coefficients for specific manure sources should be developed to provide better guidance when developing nutrient management recommendations.

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Chapter 1

A method to determine inorganic phosphorus sorption from manure to soil

Abstract

Understanding the sorption characteristics of phosphorus (P) from manure and fertilizer is important in developing nutrient management recommendations that are environmentally sustainable. Most recent P sorption research has focused on the influence of past manure application on P sorption characteristics, while very little research has been conducted on the differences in sorption characteristics where manure is used as the P source in sorption solutions. The objective of this study was to develop a method to determine if inorganic P (P_i) sorption to soils is dependent upon the source of phosphorus: Potassium phosphate (KH_2PO_4), dairy slurry, or swine slurry.

The six selected Michigan soils had no manure application history, soil test P $< 30 \text{ mg kg}^{-1}$, pH < 7 , and had a range in soil texture. The sorption procedure developed deviates from the proposed procedure of Nair et al. (1984) in that KH_2PO_4 sorption solutions were prepared in a 0.1M KCl matrix at pH 6. Nonlinear regression analysis was used to compare the standard sorption procedure of Nair et al. (1984) with the developed procedure. The two procedures, using KH_2PO_4 as the P source for sorption solutions, were similar for all soils.

Nonlinear regression analysis was used to compare P_i sorption isotherms for the different P sources. For all soils, P_i sorption capacity is significantly greater for dairy slurry than swine slurry or KH_2PO_4 . P_i sorption capacity for the swine slurry is

significantly less than KH_2PO_4 for four of the six soils. P_i sorption strength of both slurries was less than KH_2PO_4 ; however, this trend was not always significant. Based on these results, it is expected that manure from different species may increase soil test P differently. Understanding how P sorption and subsequent agronomic and environmental P availability change with manure application is necessary for sound nutrient management recommendations.

Introduction

Phosphorus (P) sorption capacity and strength of a soil have been found to change with application of manure or fertilizer. Decreased P sorption capacity and P sorption strength have been found in soils treated with manure, effluents, or superphosphate (Mozaffari and Sims, 1994; Sharpley, 1996; Holford et al., 1997; Siddique and Robinson, 2003; Laboski and Lamb, 2004). Holford et al. (1997) found that the magnitude of the decrease in sorption capacity and strength was dependent on the amount of manure or effluent applied over time. However, P sorption capacity has not always been found to decrease with manure application. Mozaffari and Sims (1994), Laboski and Lamb (2004), and Sharpley (1996) reported increases in P sorption capacity with manure application for at least one soil used in each study.

The primary focus of recent P sorption research has been to determine if manure application can change soil P sorption characteristics. This has been done by constructing sorption isotherms after application of manure, either in an incubation study or in a field setting, using KH_2PO_4 as the source of P in the isotherm characterization. Limited research has been conducted on P sorption where manure is the source of P in the sorption solutions. Bhat and O'Callaghan (1980) found that more inorganic P (P_i) sorbed to soil from solutions of pig slurry than KH_2PO_4 . However, the sorption solutions were not treated to inhibit microbial activity. Thus, it is likely that some of the observed increase in P sorption was actually microbial consumption of P. Additionally, the solution matrix, unbuffered 0.01 M KCl, had a low ionic strength and the pH was not buffered. This matrix may have permitted the pig slurry to control ionic strength and perhaps pH for some solutions over the range in P concentrations.

A standard P sorption procedure was published by Nair et al. (1984) to provide a reproducible method that would allow for comparison of isotherm coefficients from different research. This procedure uses a range of low P concentration solutions, prepared from KH_2PO_4 , in unbuffered 0.01 M CaCl_2 . If this procedure is used when manure is the source of P in the sorption solutions, precipitation of calcium (Ca) phosphates would likely occur. Generally, manure has high Ca concentrations. The addition of Ca ions in the manure sorption solution matrix would likely cause the solution to be supersaturated with respect to calcium phosphate compounds. Furthermore, an unbuffered system would likely result in solutions with pH greater than 7, further increasing the possibility of calcium phosphate precipitation if the pH is not fixed. In addition, the ionic strength of the sorption solution matrix suggested by Nair et al. (1984) is likely less than the ionic strength of diluted manure slurries. If sorption solutions with manure as the P source are prepared in unbuffered 0.01 M CaCl_2 , the ionic strength of the sorption solutions would increase as the concentration of P in solution increases because the ionic strength is being controlled by the amount of slurry used. Controlling ionic strength throughout the entire P concentration range of the sorption solutions is important because an increase in ionic strength has been shown to enhance P sorption (Ryden and Syers, 1975).

The effects of ionic strength, cation species, and pH on P sorption have been studied previously. Ryden and Syers (1975) found that ionic strength and cation species both affected P sorption when four New Zealand soils were equilibrated for 40 h with P sorption solutions with varying cations and ionic strength. They suggest that if a rapid equilibration time is desired then a solution matrix of high ionic strength with a divalent

cation should be utilized. To avoid precipitation of phosphate compounds when high P additions are used they suggest the use of a solution matrix of high ionic strength with cations of soluble phosphates such as sodium or potassium.

The objectives of this study were to (i) determine a procedure to characterize how P_i from dairy slurry and swine slurry sorbs to soil and (ii) compare how P_i sorption from dairy and swine slurries differ from the sorption of P from KH_2PO_4 . The information obtained will aid in understanding the ability of soil to sorb P directly from manure and highlight potential implications for nutrient management.

Methods and Materials

Soil and Manure

Six surface soils (0-0.15 m) used in this experiment were collected in southern, central Michigan and are described in Table 1.1. Selected soils had a range in soil texture, Bray 1-P < 30 mg kg⁻¹, and pH < 7. None of the selected soils had a history of manure application. These selection criteria were employed to find soils where initial desorption of P would be minimal and to minimize calcium phosphate precipitation. Soils were air dried, sieved (2 mm sieve), and characterized by measuring pH, organic matter, cation exchange capacity (CEC), and Bray 1-P (Brown, 1998). Soil particle size was determined by the hydrometer method (Gee and Bauder, 1986) (Table 1.1).

The liquid dairy slurry used in this experiment was collected from a short-term storage pit near the feeding facility. The pit was agitated before sample collection to insure sample homogeneity. The liquid swine slurry used in this experiment was collected from a slotted floor feeder house at time of cleaning. Once collected, manure

Table 1.1. Classification and characterization of selected surface soils.

Soil Series	Classification	pH 1:1 H ₂ O	Organic Matter ----- % -----	Silt	Clay	CEC [†] cmol _c kg ⁻¹	Bray 1-P mg kg ⁻¹
Capac	Fine-loamy, mixed, semiactive, mesic Aquic Glossudalf	6.4	2.9	32	37	31	14
Colwood 1	Fine-loamy, mixed, active, mesic Typic Endoaquoll	5.6	5.4	42	36	22	15
Colwood 2	Fine-loamy, mixed, active, mesic Typic Endoaquoll	5.3	6.1	48	40	12	8
Oshtemo	Coarse loamy, mixed, active, mesic Typic Hapludalf	5.4	2.5	68	23	9	11
Parkhill	Fine-loamy, mixed, semiactive, nonacid, mesic Mollic Endoaquepts	6.7	5.2	32	39	29	4
Spinks	Sandy, mixed, mesic Lamellic Hapludalf	4.7	4.5	76	19	5	14

[†] Cation-exchange capacity.

from each species was individually mixed and sieved (2 mm sieve) to facilitate pipetting by removing large residual particles. Manures were characterized by measuring percent moisture, percent solids, total N, total P, soluble salts (K, Ca, Mg, and Na), Al, and Fe (Peters, 2003) (Table 1.2). Manures were stored in polyethylene containers at 0 °C. Aliquots of manure from each species were thawed and stored at 4 °C as needed.

Table 1.2. Characterization of liquid dairy and swine manure slurries.

Species	Moisture	Solids	N	P	K	Ca	Mg	Na	Al	Fe
	----- % -----		----- mg L ⁻¹ -----							
Dairy	95.3	4.7	3271	529	2228	1618	539	647	21	57
Swine	94.8	5.2	6542	1294	3810	1078	648	755	53	151

Sorption Procedure Determination

The standard P sorption procedure of Nair et al. (1984) used unbuffered KH_2PO_4 solutions in 0.01 M CaCl_2 . The speciation model Phreeqc (Parkhurst, 1995) predicted that calcium phosphate compounds would precipitate at high P solution concentrations when manure chemistry was input into the model with the background solution matrix proposed by Nair et al. (1984) (unbuffered 0.01 M CaCl_2). To prevent precipitation, the sorption solution pH was fixed at the average soil pH of 6 and 0.1 M KCl was used as the background electrolyte.

The electrolyte concentration was determined by comparing the conductivity of P solutions (0, 50, 75, and 100 mg P L⁻¹) with dairy slurry or swine slurry as the P source

that were prepared in 0.05, 0.07, or 0.1 *M* KCl (Table 1.3). The necessary molarity of KCl was determined to be 0.1 *M* KCl due to low variability of electrical conductivity between solutions prepared with 0 mg total P L⁻¹ up to 100 mg total P L⁻¹ when manure was the P source.

Table 1.3. Experimental determination of background electrolyte concentration required for sorption solutions when manure slurries were diluted with various concentrations of KCl.

Manure Species	P _t [†] concentration mg P _t L ⁻¹	Electrical Conductivity		
		0.05 <i>M</i> KCl	0.07 <i>M</i> KCl	0.1 <i>M</i> KCl
		----- mS -----		
Dairy	0	4.3	5.7	7.9
	50	8.2	6.1	7.5
	75	9.0	6.1	7.5
	100	8.4	6.4	7.9
Swine	0	4.3	5.7	7.9
	50	9.1	6.4	7.9
	75	9.2	6.7	8.1
	100	10.5	7.1	8.5

[†] Approximate concentrations of total P (P_t) in each sorption solution.

Other deviations from the Nair et al. (1984) method included the addition of chloroform and filtration method. Chloroform (in 0.75% ethanol; EM Science, guaranteed reagent; Gibbstown, NJ) was added at a rate of 0.16 ml of chloroform to 25 ml of solution. This ratio is about half that proposed by Nair et al. (1984) but was experimentally determined to be adequate in suppressing microbial activity for the 24 h equilibration period (Appendix A). Nair et al. (1984) proposed the use of 0.45 µm filter paper for filtration of equilibrated solutions. However, this form of filtration is very time consuming and costly. Thus, 0.45 µm filtration units (Millex™ Millipore Corporation,

Bedford, MA) and Whatman No. 1 filter paper (Whatman International Ltd, England) were tested to determine if there were differences in P_i solution concentrations for these filtration methods. Whatman No. 1 filter paper filtration was not different than filtration with 0.45 μm filter disc units. Thus, Whatman No. 1 filter paper was found to be is adequate for filtration of equilibrated solutions, for further details see Appendix B.

To determine if variations in cation and ionic strength of the sorption solutions created sorption isotherms with different characteristics, two separate sorption experiments were conducted. First, soils were equilibrated with P solutions (ranging in concentration from 0 mg P L^{-1} to 50 mg P L^{-1}) prepared from KH_2PO_4 in unbuffered 0.01 M CaCl_2 at a 1:25 (w/v) soil to solution ratio with the addition of 0.16 ml of chloroform to 25 ml of solution to inhibit microbial activity. In the second experiment, soils were equilibrated with P solutions (ranging in concentration from 0 mg P L^{-1} to 50 mg P L^{-1}) prepared from KH_2PO_4 in 0.1 M KCl , pH 6 at a 1:25 (w/v) soil to solution ratio with the addition of 0.16 ml of chloroform to 25 ml of solution to inhibit microbial activity. In the sorption experiments, soil was equilibrated with the solutions for 24 h in an end-over-end shaker. After equilibration, samples were centrifuged for 10 min at 2350 g and filtered through Whatman No. 1 filter paper. The amount of P sorbed was determined by the difference in the concentration of P initially added and the concentration of P in solution at the end of the equilibration period. Sorption isotherms were measured in triplicate.

Sorption isotherms were fit to the Langmuir equation which is given by:

$$Q = \frac{bkC}{1 + kC} \quad (1)$$

where Q is the amount of P sorbed to the soil (mg P kg^{-1}), C is the amount of P in the solution after equilibration (mg P L^{-1}), b is the sorption maxima (mg P kg^{-1}), and k is the

sorption strength ($L\ mg^{-1}$). Nonlinear regression was used to obtain the estimates and standard errors of b and k sorption parameters. (NLIN procedure; SAS Institute, Inc., 1999). Sorption isotherms were compared using nonlinear regression to determine if changing the solution matrix changed the isotherm characteristics. The procedure used was similar to comparing regression coefficients in linear regression (Cook and Weisberg, 1999; Freud and Littell, 2000; Laboski and Lamb, 2004).

Inorganic Phosphorus Sorption Experiment

P_i sorption experiments were conducted using three different sources of P: potassium phosphate (KH_2PO_4), dairy slurry, and swine slurry. Solution P_i concentrations ranged from 0-75 $mg\ P\ kg^{-1}$ for KH_2PO_4 , 0-70 $mg\ P_i\ kg^{-1}$ for dairy slurry, and 0-60 $mg\ P_i\ kg^{-1}$ for swine slurry. Solutions were prepared in 0.1 M KCl at pH 6 (Table 1.4). P solutions were added to soil at a 1:25 (w/v) soil to solution ratio. Chloroform was added, to inhibit microbial activity, at a ratio of 0.16 ml to 25 ml of solution. Samples were equilibrated for 24 h in an end-over-end shaker and centrifuged at 2350 g for 10 minutes then filtered through Whatman No. 1 filter paper. Isotherms were measured in triplicate for each combination of soil and P source.

Daily differences in solution P_i concentrations caused by P cycling were noticed when initial P_i values were determined from solutions stored at 4 °C. Therefore, for each replication initial P_i values for each manure solution were determined in duplicate by placing 25 ml of each sorption solution and 0.16 ml of chloroform in a 50 ml centrifuge tube (Corning Inc., Life Sciences; Acton, MA) and shaking for 24 h under the same conditions as the samples (Table 1.4).

Table 1.4. Concentration of inorganic P (P_i) in each sorption solution when dairy slurry, swine slurry, and KH_2PO_4 were used as P sources.

Sorption	----- P_i^{\dagger} -----		
Solution	Dairy	Swine	KH_2PO_4
	----- $mg\ L^{-1}$ -----		
1	0	0	0
2	1.3	1.9	2
3	3.4	4.5	5
4	6.8	8.8	10
5	10.0	13.4	15
6	13.3	17.3	20
7	20.5	25.1	30
8	33.0	41.9	50
9	49.3	60.3	75
10	69.8	--	--

[†] Average initial inorganic P (P_i) concentration as measured in solutions which were not equilibrated with soil but were shaken for 24 h with 0.16 ml of chloroform to 25 ml of solution at the same time samples went through the batch equilibration process.

Samples were analyzed for P_i by the ascorbic acid colorimetric method at a wavelength of 882 nm (Frank et al., 1998). The amount of phosphorus sorbed was calculated as the difference between the concentration of P_i initially added and the concentration of P_i in solution at the end of the equilibration period. Sorption isotherms were fit to equation 1. Sorption isotherms were compared as previously described using nonlinear regression to determine if P_i sorption characteristics were different for the different P sources.

Results and Discussion

Comparison of Matrices

Sorption capacity for the two P sorption solution matrices were not significantly ($\alpha=0.05$) different for all soils (Table 1.5, Figure 1.1, 1.2, and 1.3). Sorption strength for the two solution matrices was not significantly different for all soils except Oshtemo and Colwood 2. Overall, these two solution matrices yielded sorption isotherms that were not considerably different. Hence, a matrix of 0.1 M KCl at pH 6 was used to prepare manure sorption solutions and will provide results comparable to research using an unbuffered 0.01 M CaCl_2 solution matrix.

Inorganic Phosphorus Sorption Experiment

For all soils, P_i sorption capacity (b) was significantly ($\alpha=0.05$) greater for dairy slurry than swine slurry or KH_2PO_4 (Table 1.6, Figure 1.4, 1.5, and 1.6). The increase in P_i sorption capacity observed when dairy slurry is the P source may be due to complexation of organic acids in the manure with Al and Fe from soil minerals giving rise to new P sorption sites on these complexes where hydroxyl groups are exchanged for phosphate (Appelt et al., 1975). P_i sorption capacity from the swine slurry was significantly ($\alpha=0.05$) less than that of KH_2PO_4 for four of the six soils (Capac, Colwood 2, Oshtemo, and Spinks). P_i sorption capacity from the swine slurry was not significantly ($\alpha=0.05$) different than KH_2PO_4 for Colwood 1 and Parkhill soils (Figure 1.4 and Figure 1.6). The reduction in sorption capacity from swine manure compared to KH_2PO_4 may be caused by preferential blocking of retention sites or displacement of sorbed P by anions of organic acids (Swenson et al., 1949; Kafkafi et al., 1998).

Table 1.5. Comparison of Langmuir parameters for standard and developed P sorption matrices.

Soil Series	Sorption Solution Matrix	----- Langmuir Parameters -----		
		<i>b</i>	<i>k</i>	R ²
		mg kg ⁻¹	L mg ⁻¹	
Capac	CaCl ₂ [†]	265a [§]	0.270a	0.97
	KCl [‡]	261a	0.201a	0.96
Colwood 1	CaCl ₂	476a	0.217a	0.98
	KCl	481a	0.175a	0.98
Colwood 2	CaCl ₂	175a	0.070a	0.97
	KCl	207a	0.038b	0.99
Oshtemo	CaCl ₂	106a	0.231a	0.96
	KCl	109a	0.141b	0.97
Parkhill	CaCl ₂	329a	0.200a	0.96
	CaCl ₂	294a	0.180a	0.96
Spinks	KCl	369a	0.311a	0.97
	CaCl ₂	363a	0.301a	0.97

[†] CaCl₂ = standard matrix = unbuffered 0.01 M CaCl₂

[‡] KCl = developed matrix = 0.1 M KCl at pH 6.0

[§] Within a soil series, rows within a column followed by the same letter are not significantly different ($\alpha=0.05$) from one another.

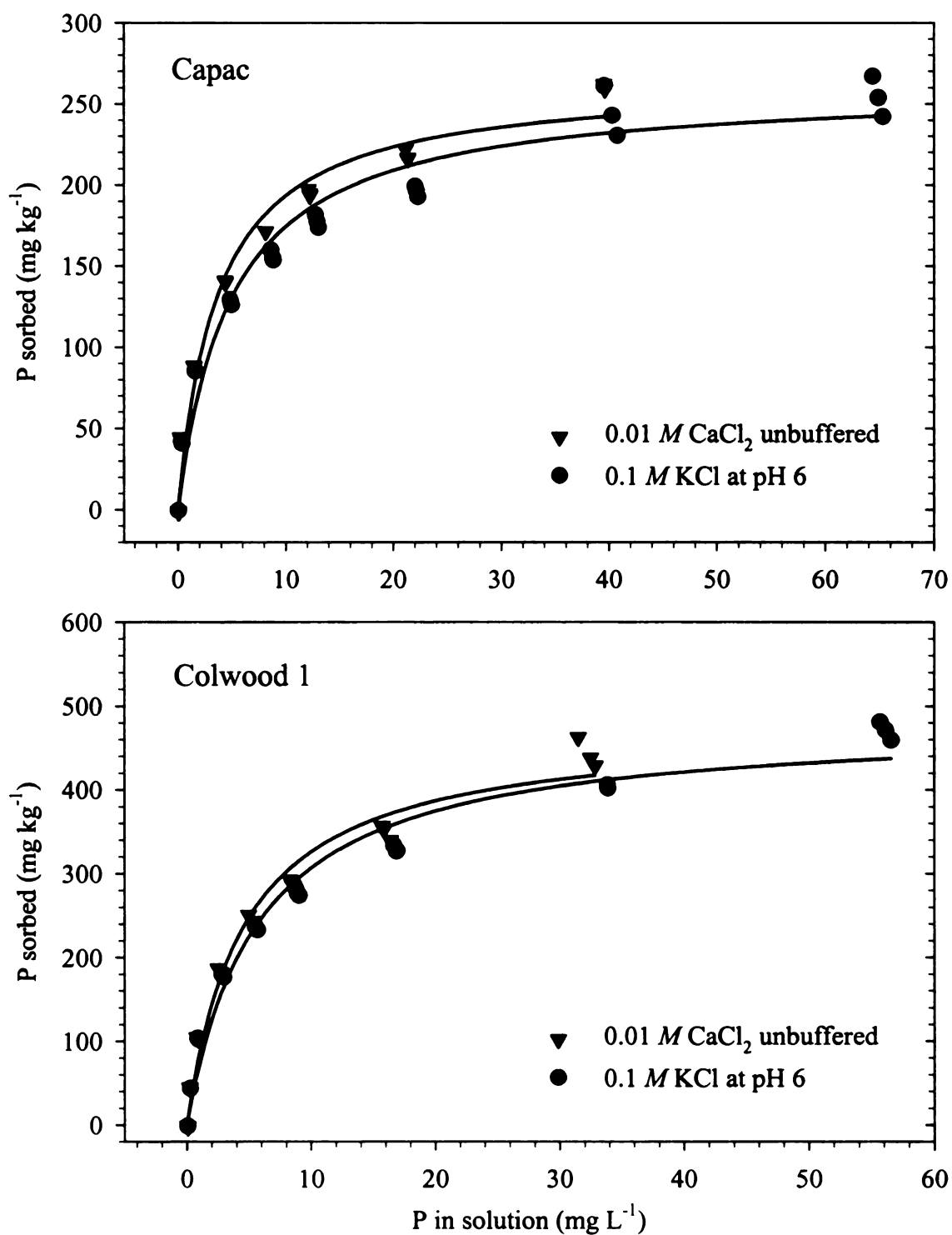


Figure 1.1. Sorption isotherms for CaCl_2 and KCl sorption solution matrices for the Capac and Colwood 1 soils when KH_2PO_4 was used as the source of P.

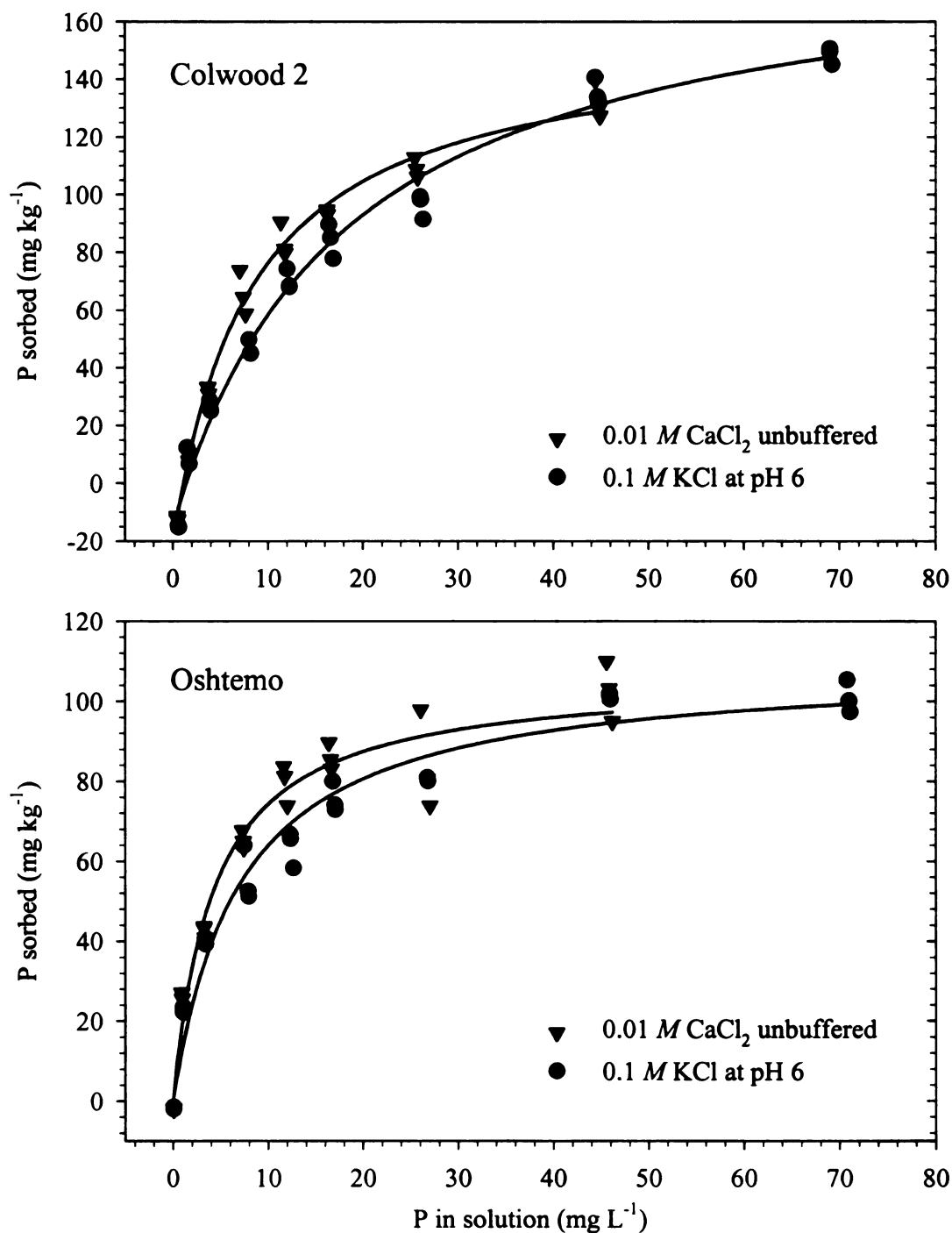


Figure 1.2. Sorption isotherms for CaCl₂ and KCl sorption solution matrices for the Colwood 2 and Oshtemo soils when KH₂PO₄ was used as the source of P.

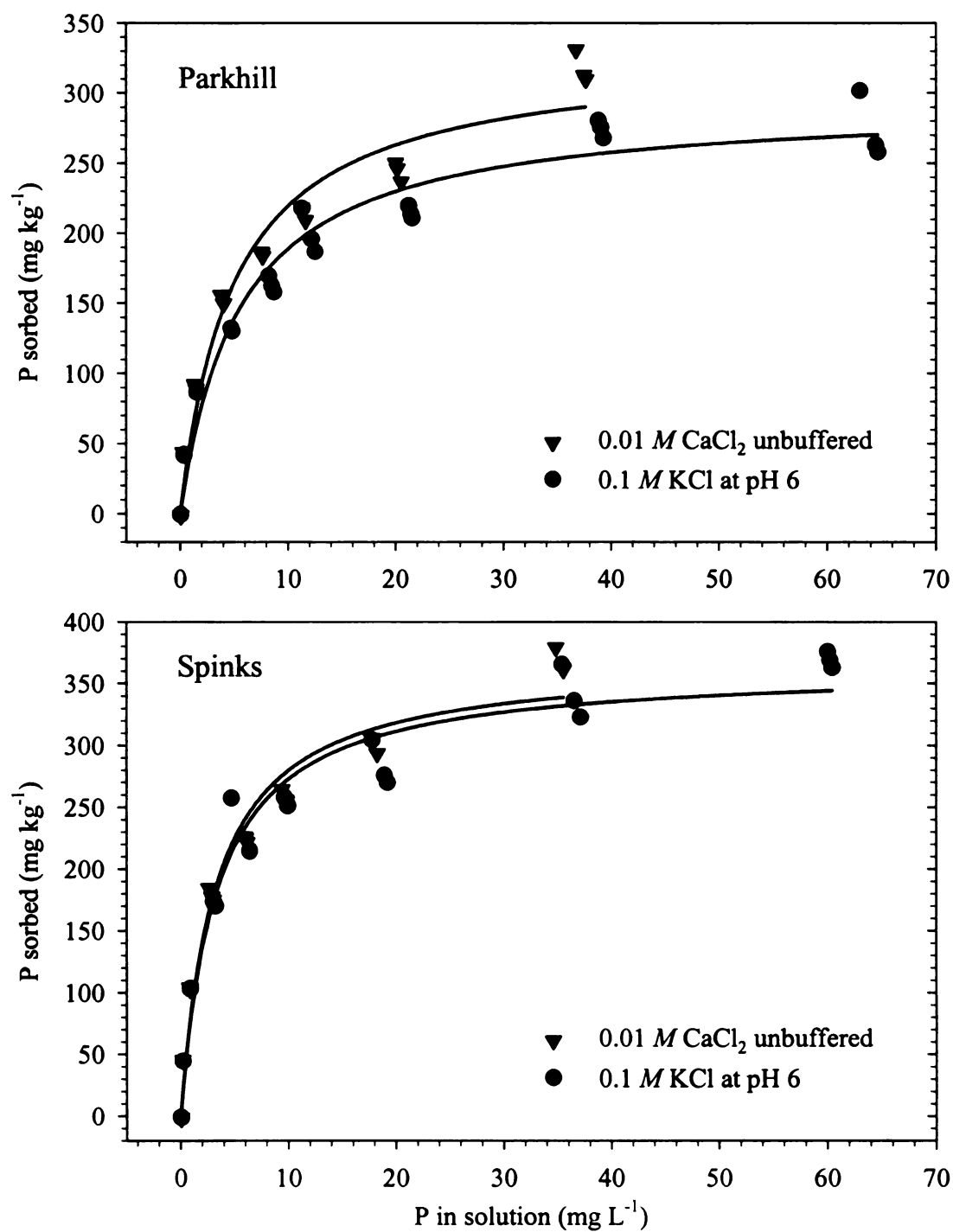


Figure 1.3. Sorption isotherms for CaCl₂ and KCl sorption solution matrices for the Parkhill and Spinks soils when KH₂PO₄ was used as the source of P.

Table 1.6. Effect of inorganic P (P_i) source on Langmuir parameters.

Soil Series	Source	----- Langmuir Parameters -----		
		b	k	R^2
		mg kg ⁻¹	L mg ⁻¹	
Capac	KH ₂ PO ₄	261a [†]	0.201a	0.96
	Dairy	329b	0.135b	0.95
	Swine	172c	0.180ab	0.97
Colwood 1	KH ₂ PO ₄	481a	0.175a	0.98
	Dairy	713b	0.107b	0.97
	Swine	318c	0.175a	0.98
Colwood 2	KH ₂ PO ₄	205a	0.056a	0.99
	Dairy	327b	0.049ab	0.98
	Swine	187c	0.042b	0.99
Oshtemo	KH ₂ PO ₄	109a	0.141a	0.97
	Dairy	144b	0.123a	0.95
	Swine	114a	0.063b	0.96
Parkhill	KH ₂ PO ₄	294a	0.180a	0.96
	Dairy	374b	0.098b	0.96
	Swine	191c	0.146ab	0.97
Spinks	KH ₂ PO ₄	363a	0.301a	0.97
	Dairy	671b	0.011b	0.96
	Swine	272c	0.225a	0.98

[†]Within a soil series, rows within a column followed by the same letter are not significantly different ($\alpha=0.05$) from one another.

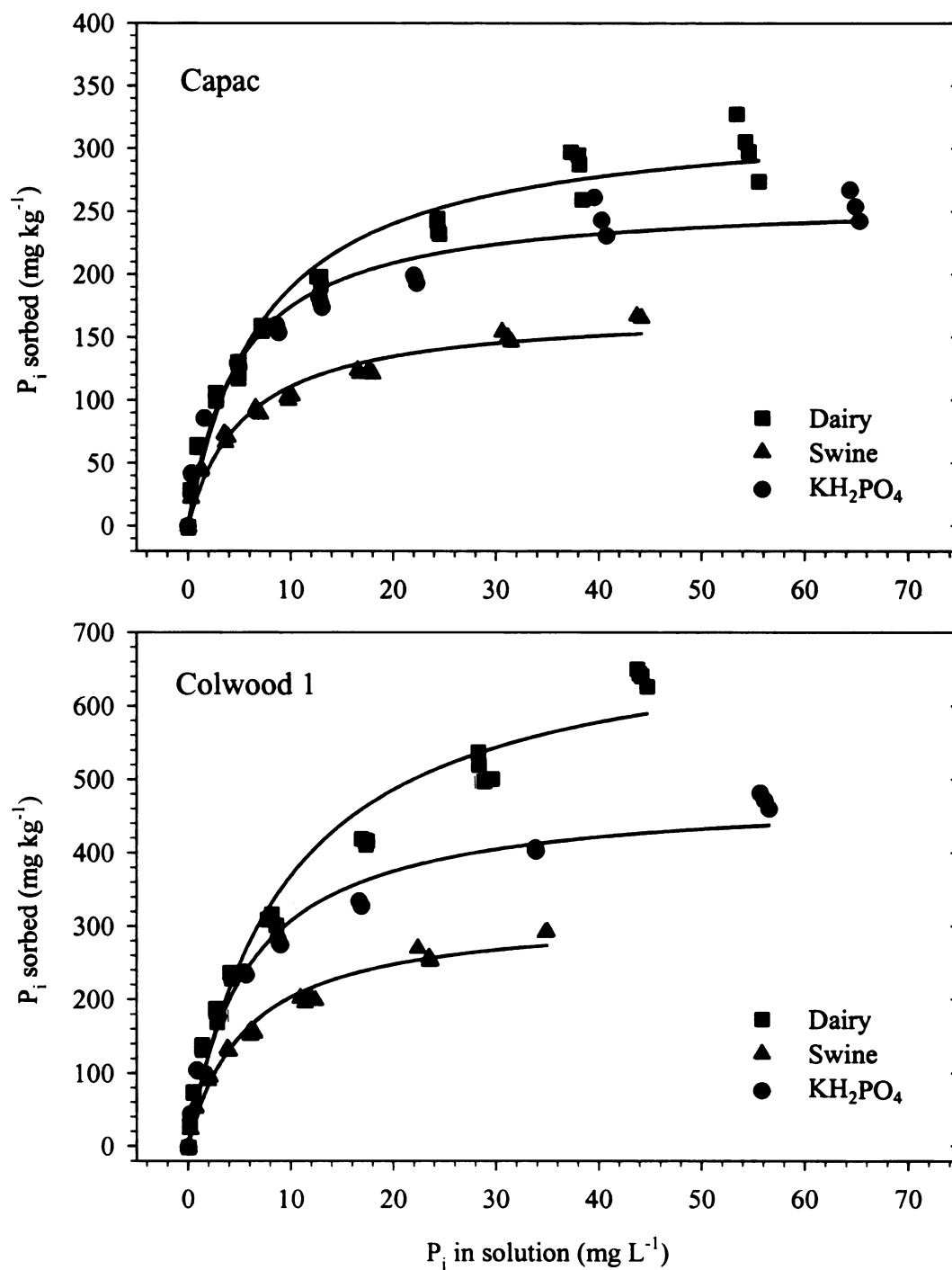


Figure 1.4. Inorganic P (P_i) sorption isotherms for the Capac and Colwood 1 soils when various concentrations and sources of P (dairy slurry, swine slurry, KH_2PO_4) were equilibrated with soil in a 0.1 M KCl, pH 6 matrix.

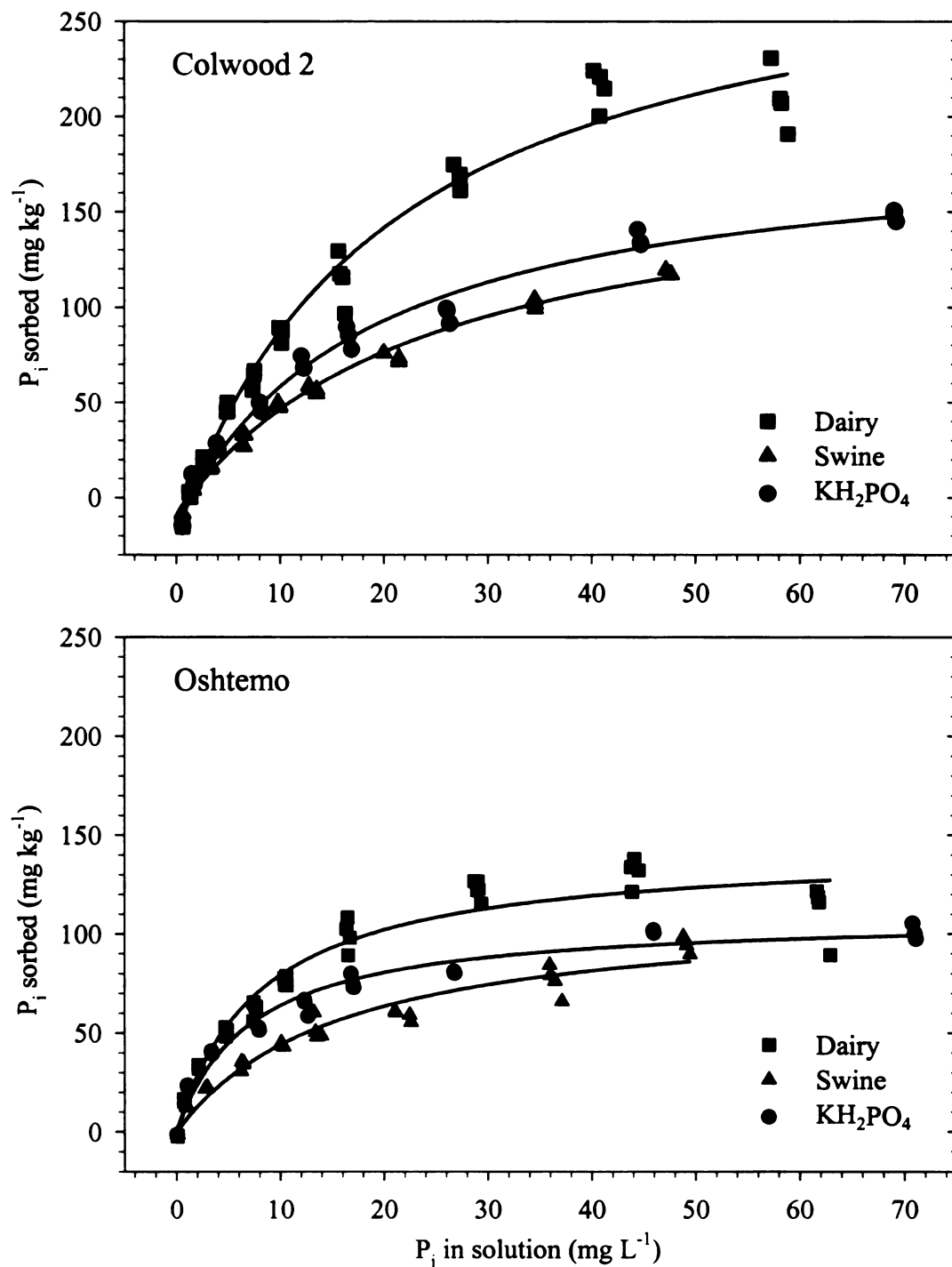


Figure 1.5. Inorganic P (P_i) sorption isotherms for the Colwood 2 and Oshtemo soils when various concentrations and sources of P (dairy slurry, swine slurry, KH_2PO_4) were equilibrated with soil in a 0.1 M KCl, pH 6 matrix.

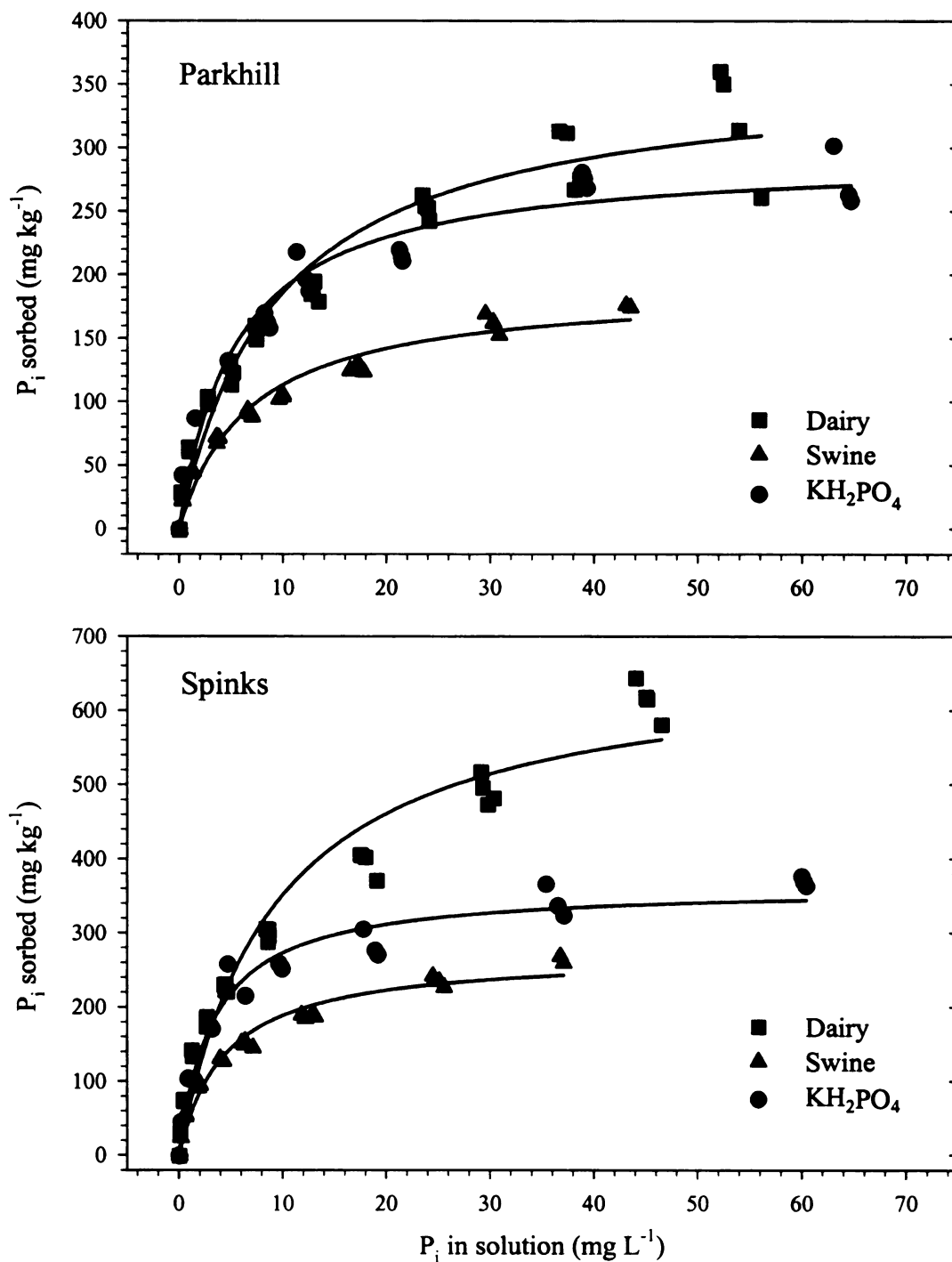


Figure 1.6. Inorganic P (P_i) sorption isotherms for the Parkhill and Spinks soils when various concentrations and sources of P (dairy slurry, swine slurry, KH_2PO_4) were equilibrated with soil in a 0.1 M KCl, pH 6 matrix.

Sorption strength (k) of the dairy slurry was significantly ($\alpha=0.05$) less than KH_2PO_4 for Colwood 1 and Spinks soils (Table 1.6). For all other soils, P_i sorption strength was not significantly different between dairy slurry and KH_2PO_4 . Sorption strength of swine slurry was significantly less than KH_2PO_4 for Capac, Colwood 2, and Oshtemo soils. For all other soils, P_i sorption strength of swine slurry and KH_2PO_4 were the same. Sorption strength of dairy slurry was not significantly different than swine slurry for Capac, Colwood 2, and Parkhill soils. Sorption strength of dairy slurry was significantly less than swine slurry for Colwood 1 and Spinks soils and was significantly greater for Oshtemo soil. Overall, P_i sorption strength of either manure slurry was less than KH_2PO_4 ; however this trend was not always significant. This observed reduction in sorption strength may be caused by the interferences of other compounds in the manure slurry with sorption of P_i at high strength sorption sites causing P_i to be sorbed to low strength sites (Holford et al., 1997).

Conclusions

Generally, soils had a greater sorption capacity for P_i from dairy slurry compared to KH_2PO_4 or swine slurry. Manure slurries tended to have a lower P_i sorption strength than KH_2PO_4 and therefore, may present an increased risk for P losses to runoff and leaching. Based on these data, it appears that the addition of swine slurry to soil will result in P being more available, as measured by soil test, than when P is added as KH_2PO_4 , because less P is sorbing to the soil and the sorption strength is weaker. On the other hand, availability of P from dairy slurry may be less than KH_2PO_4 because more P_i sorbs to soil from dairy slurry compared to KH_2PO_4 . Thus, manure from different animal species may increase soil test P levels differently.

Data from an incubation study with five of these soils support the conclusions above. Dairy slurry was always less available (as measured by soil test) than KH_2PO_4 or swine slurry whereas, swine slurry was as available as KH_2PO_4 for two soils and less available for the other three soils. See Chapter 3 for more details. The sorption isotherm data presented in this chapter may also explain why Laboski and Lamb (2003) found that swine slurry increased soil test P more than KH_2PO_4 when incubated with soil at the same rate of total P. Understanding how P sorption and subsequent agronomic and environmental availability change with manure application is necessary to develop sound nutrient management recommendations.

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Chapter 2

Sorption of inorganic and total phosphorus from dairy slurry, swine slurry, and potassium phosphate to selected Michigan soils

Abstract

Phosphorus (P) is essential for crop production but is of environmental concern with regard to surface water pollution. Little research has focused on the construction of P sorption isotherms where the P source is manure. The objective of this study was to determine and compare the sorption characteristics of inorganic P (P_i) and total P (P_t) where the P source was dairy slurry, swine slurry, or potassium phosphate (KH_2PO_4).

The six selected Michigan soils had no manure application history, soil test P < 30 ppm, pH < 7, and had a range in soil texture. Sorption solutions were prepared in 0.1 M KCl at pH 6 and equilibrated with soils at a 1:25 (w/v) soil to solution ratio for 24 h. The amount of P_i , P_t , iron (Fe) and aluminum (Al) remaining in solution were measured.

For all soils, P_i and P_t sorption capacity of dairy slurry was greater than KH_2PO_4 . P_t sorption capacity of swine slurry was greater than KH_2PO_4 , while P_i sorption capacity was less than KH_2PO_4 . Overall, P_i and P_t sorption strengths of the manure slurries were less than or equal to KH_2PO_4 . Desorbed Fe and Al were correlated to the differences in P_i sorption between dairy slurry and KH_2PO_4 but were not correlated to the differences in P_i sorption between swine slurry and KH_2PO_4 . Desorption of Fe and Al from the soil surfaces may have been caused by organic acids. The greater soil sorption capacity for P from dairy slurry may suggest that P from dairy slurry would be less available, as

measured by soil test, than fertilizer P. The reduced P sorption capacity from swine slurry suggests that swine slurry P might be more available than fertilizer P. The results also suggest that dairy slurry having lower sorption strength than swine slurry and KH_2PO_4 may have a greater potential to release P into runoff waters and/or leach. Further investigation is needed to determine the potential for P to release to surface water runoff when these manures are applied to soil.

Introduction

In 2000, the U.S. EPA reported that agriculture was the leading source of surface water pollution, affecting 18% of the assessed rivers, streams, and lakes. Agriculture contributed to approximately 45% of the reported water quality problems in impaired rivers, streams, and lakes (U.S. EPA, 2000). This is less than the 1994 estimate that agriculture contributed to 70% of the impairment in the water quality of rivers and lakes (U.S. EPA, 1994). However, further reducing pollution from agriculture is required to improve the quality of our waters.

Studies have shown that excessive application of phosphorus (P) in the form of animal manure and/or inorganic fertilizer is responsible for the accumulation of soil P to levels in excess of crop requirements (Sharpley et al., 1984; Sims, 1993). Such soils present a risk to water quality if the P is transported to surface water and accelerates eutrophication. Eutrophication has the potential to impair water quality by restricting a water body's use for fisheries, recreation, industry, and drinking purposes (Sharpley and Menzel, 1987; Sharpley et al., 1998). Phosphorus is strongly adsorbed by most soils, thus, loss of P in surface runoff is generally of greater concern than leaching (Sharpley et al., 1998). Runoff water contains P in both soluble (dissolved) and particulate (sediment bound) forms of P (Sharpley et al., 1998). Phosphorus sorption characteristics, such as sorption capacity and sorption strength, of a given soil likely affect the potential for P losses to surface waters both as soluble and particulate P. To reduce the environmental impact of P from agricultural soils, it is important to understand the mechanisms of P sorption (binding) to soil colloid surfaces.

The focus of recent P sorption research has been to construct P sorption isotherms, using solutions of KH_2PO_4 , to determine if soil P sorption characteristics change after application of manure or fertilizer compared to untreated soils. In general, P sorption capacity and strength have been found to change with the application of manure or fertilizer, with reductions in both properties more common than increases (Mozaffari and Sims, 1994; Sharpley, 1996; Holford et al., 1997; Siddique and Robinson, 2003; Laboski and Lamb, 2004). Manure application increased, reduced, or did not change sorption capacities of seven Minnesota soils (Laboski and Lamb, 2004). The authors also reported reduced or unchanged sorption strength for these soils when soils with a history of manure application were compared with the same soils to which no manure was applied (Laboski and Lamb, 2004). In another study, P sorption capacity and strength were reduced when soils were treated with manures from various species, sewage effluent, or superphosphate (Holford et al., 1997). The magnitude of the decrease in sorption capacity and strength depended on the amount of manure or effluent applied over time; with increased application rates causing a greater reduction in the sorption capacity and strength (Holford et al., 1997).

The observed decreases in P sorption capacity have been suggested by several researchers to be due to anions of organic acids competing for P sorption sites (Swenson et al., 1949; Nagarjah et al., 1970; Kafkafi et al., 1998). When organic amendments are added to soils, organic acids may be added as part of this amendment directly and/or as a result of microbial decomposition of the amendment. Reduction of P sorption can be caused by the preferential blocking of retention sites or by displacement of sorbed P by anions of these organic acids (Swenson et al., 1949; Kafkafi et al., 1998). Nagarjah et al.

(1970) found the decrease in P sorption by organic acids is dependent on the stability of the complexes formed with Fe and Al. Inositol hexaphosphate (IHP), a form of organic P in animal manures, was found to preferentially sorb to soil compared to inorganic P (Anderson et al., 1974). IHP also released orthophosphate, which was previously bound to soil, into solution when added to soil alone (Anderson et al., 1974). Additionally, as the concentration of added IHP increased, Fe and Al solution concentrations increased, whereas, the absolute amount of IHP sorbed decreased. This was probably caused by the formation of soluble complexes of Fe and Al with IHP (Anderson et al., 1974). These studies suggest that organic P (P_o) in manures may compete for binding sites on soil surfaces and potentially reduce inorganic P (P_i) sorption.

The increase in sorption capacity observed in previously mentioned research is less well understood. Appelt et al. (1975) suggested increases in P sorption capacity may be caused by complexation of organic acids with Al and Fe from soil minerals giving rise to new P sorption sites on the complexes where hydroxyl groups are exchanged for phosphate. Whereas, others found that low molecular weight organic acids increase solubility of solid-phase Al in soils (Stumm, 1986; Fox et al., 1990). Organic acids influence the release of P and Al from surfaces in soils by formation of stable complexes with Al, which is dependent on the stability constant of the ligand (Fox et al., 1990). The dissolution of Al containing solids may give rise to new P sorption sites on the freshly scoured soil surfaces.

Sorption strength estimated from the Langmuir equation was described by Holford et al. (1997) as an average strength of the total sorption sites which includes both high and low strength binding sites in the soil. Holford et al. (1997) suggested that P

initially sorbs to high strength sites followed by low bonding strength sites. They estimated that high strength sites represent approximately one-fourth of the total sites and have a bonding strength about 100 times greater than low strength sites (Holford et al., 1974).

Some authors have reported a reduction in sorption strength with the application of amendments but few have given explanations as to why this reduction in sorption strength likely occurs (Mozaffari and Sims, 1994; Sharpley, 1996; Holford et al., 1997; Siddique and Robinson, 2003; Laboski and Lamb, 2004). Holford et al. (1997) suggested that the observed reduction in sorption strength with manure or effluent application history was likely caused by organic anion interaction with sorbing P anions; thus, lowering the sorption strength. Both Holford et al. (1997) and Laboski and Lamb (2004) concluded that P sorption strength may have a greater impact on P availability than P sorption capacity and is possibly the more environmentally important sorption parameter because the reduction in P sorption strength with application of amendments resulted in a greater amount of P in soil solution at any given level of P sorbed.

Far less research has been conducted on the sorption of P where isotherms were determined using sorption solutions containing manure as the source of P. Bhat and O'Callaghan (1980) studied the P sorption characteristics of pig slurry compared to KH_2PO_4 . They found that more P_i sorbed to soil from solutions of pig slurry than KH_2PO_4 . However, the sorption solutions were not treated to inhibit microbial activity. As a result, it is likely that some of the observed increase in P sorption was actually microbial consumption of P. The objective of this study was to determine and compare

sorption characteristics of total P (P_t), inorganic P (P_i), and organic P (P_o) from dairy slurry, swine slurry, and KH_2PO_4 .

Methods and Materials

Soil and Manure

Six surface soils (0-0.15 m) used in these experiments were collected in southern, central Michigan and are described in Table 2.1. Soils selected had no history of manure application, Bray 1-P < 30 mg P kg⁻¹, pH < 7, and varied in soil texture. These selection criteria were employed to reduce initial desorption of P and minimize calcium phosphate precipitation. Prior to experimentation, soils were air dried, sieved (2 mm sieve) and mixed thoroughly to ensure homogeneity. Soils were characterized by measuring pH, organic matter, cation exchange capacity, and Bray 1-P (Brown, 1998). Soil particle size was determined by the hydrometer method (Gee and Bauder, 1986) (Table 2.1).

The liquid dairy slurry used in this experiment was collected from a short-term storage pit near a feeding facility. The pit was agitated prior to sample collection to ensure sample homogeneity. The liquid swine slurry used in this experiment was collected from a slotted floor feeder house at time of cleaning. Once collected, manures were individually mixed and sieved (2 mm sieve) to facilitate pipetting by removing large residual particles. Manures were characterized by measuring percent moisture, percent solids, total N, total P, soluble salts (K, Ca, Mg, and Na), Al, and Fe (Table 2.2) (Peters, 2003). After collection and sieving, manures were stored in polyethylene containers at 0 °C. Aliquots of manure from each species were thawed and stored at 4 °C as needed.

Table 2.1. Classification and characterization of selected surface soils.

Soil Series	Classification	pH 1:1 H ₂ O	Organic Matter	Sand ----- % -----	Silt	Clay	CEC [†] cmol _c kg ⁻¹	Bray 1-P mg kg ⁻¹
Capac	Fine-loamy, mixed, semiactive, mesic Aquic Glossudalf	6.4	2.9	32	37	31	11.7	14
Colwood 1	Fine-loamy, mixed, active, mesic Typic Endoaquoll	5.6	5.4	42	36	22	16.4	15
Colwood 2	Fine-loamy, mixed, active, mesic Typic Endoaquoll	5.3	6.1	48	40	12	16.9	8
Oshtemo	Coarse loamy, mixed, active, mesic Typic Hapludalf	5.4	2.5	68	23	9	8.3	11
Parkhill	Fine-loamy, mixed, semiactive, nonacid, mesic Mollic Endoaquepts	6.7	5.2	32	39	29	20.1	4
Spinks	Sandy, mixed, mesic Lamellic Hapludalf	4.7	4.5	76	19	5	5.4	14

[†] Cation-exchange capacity.

Table 2.2. Characterization of dairy and swine manure slurries.

Species	Moisture	Solids	N	P	K	Ca	Mg	Na	Al	Fe
	----- % -----		----- mg L ⁻¹ -----							
Dairy	95.3	4.7	3271	529	2228	1618	539	647	21	57
Swine	94.8	5.2	6542	1294	3810	1078	648	755	53	151

Phosphorus Sorption Isotherms

P sorption experiments. P sorption experiments were conducted using three different sources of P: KH_2PO_4 , dairy slurry, and swine slurry. Sorption solutions were prepared on an approximate P_i basis, using the nutrient characteristics of whole sieved manures, to contain a range of P concentrations between 0 and 100 mg $\text{P}_i \text{ L}^{-1}$ (Table 2.2). Actual solution P_i concentrations ranged from 0-75 mg P L^{-1} for KH_2PO_4 , 0-70 mg $\text{P}_i \text{ L}^{-1}$ for dairy slurry, and 0-60 mg $\text{P}_i \text{ L}^{-1}$ for swine slurry (Table 2.3). Solutions were prepared in 0.1 M KCl at pH 6 (See Chapter 1 for details). P sorption solutions were added to soil at a 1:25 (w/v) soil to solution ratio. Chloroform (in 0.75% ethanol; guaranteed reagent; EM Science, Gibbstown, NJ) was added to inhibit microbial activity at a rate of 0.16 ml of chloroform to 25 ml of solution (Appendix A). Solutions were equilibrated for 24 h in an end-over-end shaker.

Daily differences in solution P_i concentrations caused by P cycling were noticed when initial P_i solution concentrations were determined from solutions stored at 4 °C. Therefore, for each replication initial P_i and P_f values for each manure sorption solution were determined in duplicate by placing 25 ml of each sorption solution in a 50 ml centrifuge tube (Corning Inc., Life Sciences; Acton, MA) with no soil (Table 2.3).

Table 2.3. Phosphorus sorption solution characterization.

Sorption Solution	----- Dairy -----			----- Swine -----			KH ₂ PO ₄
	P _i [†]	P _t [‡]	P _i as percent of P _t	P _i [†]	P _t [‡]	P _i as percent of P _t	P
	--- mg L ⁻¹ ---		%	--- mg L ⁻¹ ---		%	mg L ⁻¹
1	0	0		0	0		0
2	1.3	1.6	81	1.9	2.0	95	2
3	3.4	4.0	85	4.5	4.7	96	5
4	6.8	7.9	86	8.8	9.1	97	10
5	10.0	11.8	85	13.4	14.0	96	15
6	13.3	15.3	87	17.3	18.0	96	20
7	20.5	23.0	89	25.1	26.5	95	30
8	33.0	37.8	87	41.9	42.9	98	50
9	49.3	57.3	86	60.3	63.1	96	75
10	69.8	70.1	100	--	--	--	--

[†] Average (eight replications) initial inorganic P (P_i) solution concentration of centrifuged samples.

[‡] Average (eight replications) initial total P (P_t) solution concentration, of centrifuged samples.

Solutions were shaken for 24 h under the same conditions as the samples. After equilibration, all samples, including those for measurement of initial P_i and P_t concentrations, were centrifuged at 2350 g for 10 minutes. It was assumed that similar amounts of manure P would be removed by centrifugation with and without the presence of soil. The percent P_i and P_t removed from manure sorption solutions by centrifugation was determined in a separate experiment, see Appendix C for details. The amount of P_i as a percent of P_t is similar across the solution range for a given slurry showing that centrifugation removed similar percents of P_o in these solutions (Table 2.3).

P_i analysis. After centrifugation, an aliquot of solution was reserved for P_i digestion. The remaining solution was then filtered through Whatman No. 1 filter paper (Whatman International Ltd, England) (Appendix B) for P_i sorption analysis. All

samples were analyzed for P_i immediately after equilibration by the ascorbic acid **c**olorimetric method at a wavelength of 882 nm (Frank et al., 1998). The amount of P_i **s**orbed was determined by the difference between the concentration of P_i initially added **a**nd the concentration of P_i in solution at the end of the equilibration period.

P_i analysis. Reserved aliquots of unfiltered equilibrated sorption solutions were **i**mmediately stored at 4 °C until digestion for P_i analysis. Samples were digested **a**ccording to the persulfate oxidation method of Bender and Wood (2000) with some **m**odifications. Aliquots of equilibrated samples (5 or 10 ml) were diluted to a final **v**olume of 50 ml with distilled water. Diluted samples were then digested with 0.7 g **p**otassium persulfate and 1 ml of 11 *N* H_2SO_4 . The optimum potassium persulfate needed **f**or complete digestion was determined in a separate experiment, see Appendix D for **d**etails. Samples were first digested for 1.25 h at approximately 100 °C, and then the **h**otplate was turned to the maximum setting, to increase boiling, until the samples were **r**educed to approximately 10 ml. Cooled samples were diluted with 30 ml of distilled **w**ater. After samples were diluted, approximately 5 ml of 2 *M* NaOH was added to adjust **t**he pH of the solution. Solutions were transferred to volumetric flasks and diluted to a **f**inal volume of 100 ml. Phosphorus in diluted digested samples was analyzed by the **a**scorbic acid colorimetric method at a wavelength of 882 nm (Frank et al., 1998). **D**igested standards of KH_2PO_4 were used to produce the standard curve for determination **o**f the concentration of P_i in solution. The amount of P_i sorbed was determined by the **d**ifference between the concentration of P_i initially added and the concentration of P_i in **s**olution at the end of the equilibration period.

P_o analysis. The amount of P_o sorbed was determined by the difference between the amount of P_i and P_f sorbed. Likewise, the amount of P_o remaining in solution after equilibration was determined by the difference between the amount of P_i in solution and the amount of P_f in solution.

Iron and Aluminum Solution Concentrations

Aliquots of equilibrated solutions used for P_i analysis also were analyzed for Fe and Al concentrations in solution to determine if manure slurry solutions caused dissolution of Fe and Al from soil colloid surfaces. Samples were spiked with 5 mg L⁻¹ each of Fe and Al to achieve values above the 1 mg L⁻¹ method detection limit. Spiked samples were analyzed for Fe and Al in solution using a direct current plasma spectrometer (DCP) (SpectraSpan V; Andover, MA). The amount of Fe and Al desorbed was calculated by the difference between the amount of Fe and Al in solution initially and the amount in solution after equilibration.

Data Analysis

P Sorption Isotherms. Nonlinear regression was used to fit P_i and P_f sorption data to the Langmuir equation which is given by:

$$Q = \frac{bkC}{1 + kC} \quad (1)$$

where Q is the amount of P sorbed to the soil (mg P kg⁻¹), C is the amount of P in the solution after equilibration (mg P L⁻¹), b is the sorption maxima (mg P kg⁻¹), and k is the sorption strength (L mg⁻¹). Nonlinear regression was used to obtain estimates and standard errors of the b and k parameters (NLIN procedure; SAS Institute, Inc., 1999).

Comparisons of b and k terms between two data sets were made using nonlinear regression in a procedure similar to comparing regression coefficients in linear regression (Cook and Weisberg, 1999; Freud and Littell, 2000; Laboski and Lamb, 2004). The P_o sorption isotherms did not fit the Langmuir equation.

Relationship Between Phosphorus and Iron and Aluminum. As shown in Chapter 1, for a given soil there were significant differences in P_i sorption capacities for the different P sources. However, P_i sorption capacities for the dairy and swine slurries were not considerably different from one another and were greater than the sorption capacity of KH_2PO_4 . In order to investigate whether those differences in either P_i or P_t sorption capacities were related to desorption of Fe or Al from soil surfaces, the following analysis was employed. First, because discrete data points for the three P sources at precisely the same solution P concentrations did not exist, Q values for KH_2PO_4 were computed by substituting the experimentally determined C values of a given slurry in the Langmuir equation for sorption from KH_2PO_4 for each data point from the manure slurries. These calculated KH_2PO_4 - Q values were then subtracted from the experimentally derived Q values for the respective slurry to obtain the difference in P_i or P_t sorbed between the slurries and KH_2PO_4 . Next, the Fe and Al desorbed during the equilibration of each slurry-soil sample were correlated with the differences in P_i or P_t sorption calculated in the first step.

Results and Discussion

Iron and Aluminum Solution Concentrations

For all soils, Fe and Al desorbed from soil constituents for both slurries with more desorption occurring in soils equilibrated with dairy slurry compared to swine slurry. (Appendix E). No apparent desorption of Fe and Al occurs when soils are equilibrated with KH_2PO_4 solutions (Appendix E). Difference in dissolution of Fe and Al for the two manure sources may be caused by differences in the concentrations and type of organic acids in the different manure species; Fox et al. (1990) found these factors impact solubility of solid phase Al in soils. Organic acid type and concentration was not measured for the manures used in this study. However, differences in organic acid compositions between the manures could likely occur and be caused by differences in animal diet, physiology, and perhaps manure storage.

Phosphorus Sorption Capacity

For all soils, P_i sorption capacity (b) was significantly ($\alpha=0.05$) greater for dairy slurry than swine slurry or KH_2PO_4 (Table 2.4, Figure 2.1, 2.2, 2.3, 2.4, 2.5, and 2.6). P_i sorption capacity for the swine slurry was significantly less than that of KH_2PO_4 for Capac, Oshtemo, and Spinks soils, but was not significantly different than KH_2PO_4 for Colwood 1, Colwood 2, and Parkhill soils.

For all soils, P_i sorption capacity was significantly greater for both dairy and swine slurries compared to KH_2PO_4 (Table 2.4). For Capac, Colwood 1, and Spinks soils, P_i sorption capacity was significantly greater for dairy slurry than swine slurry, but dairy slurry was not significantly different than swine slurry for all other soils.

Table 2.4. Effect of P source on Langmuir parameters for selected soils.

Soil Series	Source	---- Langmuir Parameters ----		
		<i>b</i>	<i>k</i>	R ²
		mg kg ⁻¹	L mg ⁻¹	
Capac	P _i KH ₂ PO ₄	261a [†]	0.201a	0.96
	P _i Dairy	329b	0.135b	0.95
	P _t Dairy	439c	0.087c	0.94
	P _i Swine	172d	0.180abc	0.97
	P _t Swine	297e	0.238a	0.95
Colwood 1	P _i KH ₂ PO ₄	481a	0.175a	0.98
	P _i Dairy	713b	0.107b	0.97
	P _t Dairy	741b	0.089b	0.98
	P _i Swine	318c	0.175a	0.98
	P _t Swine	604d	0.161a	0.97
Colwood 2	P _i KH ₂ PO ₄	207a	0.038a	0.99
	P _i Dairy	362b	0.105a	0.98
	P _t Dairy	577c	0.016b	0.98
	P _i Swine	212a	0.027ab	0.99
	P _t Swine	676c	0.012b	0.96
Oshtemo	P _i KH ₂ PO ₄	109a	0.141a	0.97
	P _i Dairy	144b	0.123a	0.95
	P _t Dairy	181c	0.091b	0.98
	P _i Swine	114a	0.063c	0.96
	P _t Swine	181c	0.091abc	0.91
Parkhill	P _i KH ₂ PO ₄	294a	0.180a	0.96
	P _i Dairy	374b	0.098b	0.96
	P _t Dairy	437c	0.081b	0.95
	P _i Swine	191d	0.146ab	0.97
	P _t Swine	394bc	0.115b	0.93
Spinks	P _i KH ₂ PO ₄	363a	0.301a	0.97
	P _i Dairy	671b	0.109b	0.96
	P _t Dairy	692b	0.081b	0.97
	P _i Swine	272c	0.225ac	0.98
	P _t Swine	517d	0.179c	0.97

[†] For a given soil, values within a column followed by the same letter are not significantly different at $\alpha=0.05$.

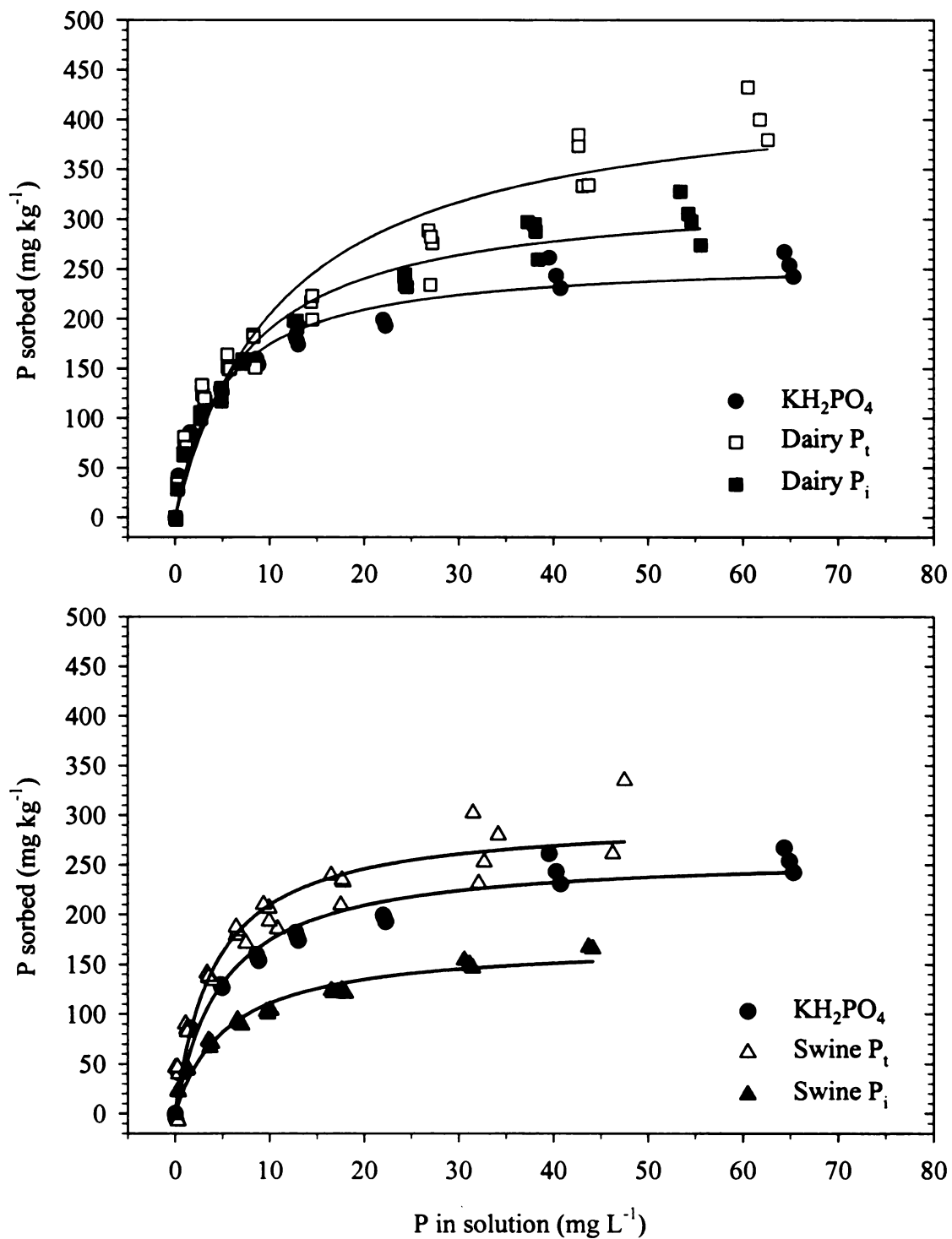


Figure 2.1. Inorganic P (P_i) and total P (P_t) sorption isotherms for Capac soil.

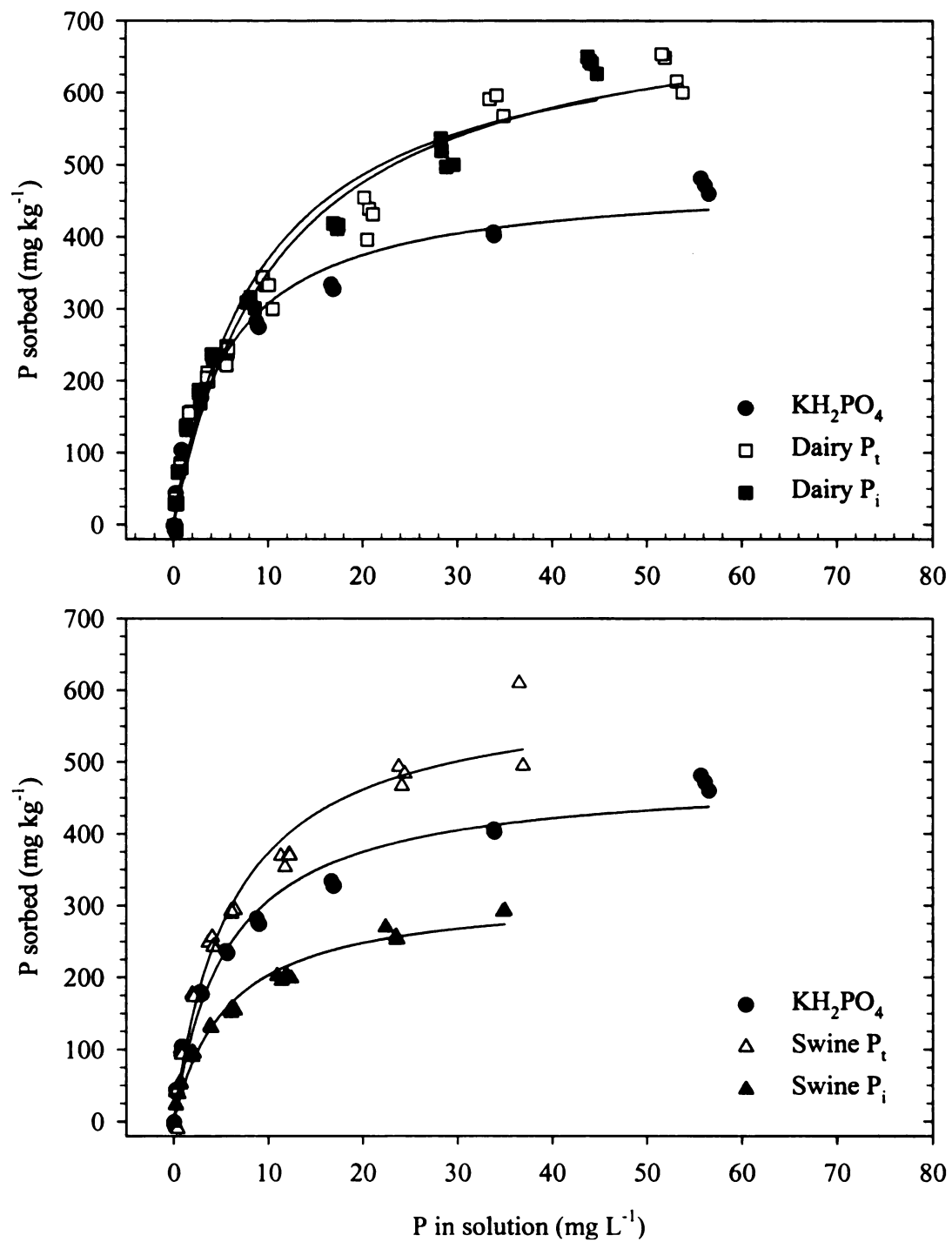


Figure 2.2. Inorganic P (P_i) and total P (P_t) sorption isotherms for Colwood 1 soil.

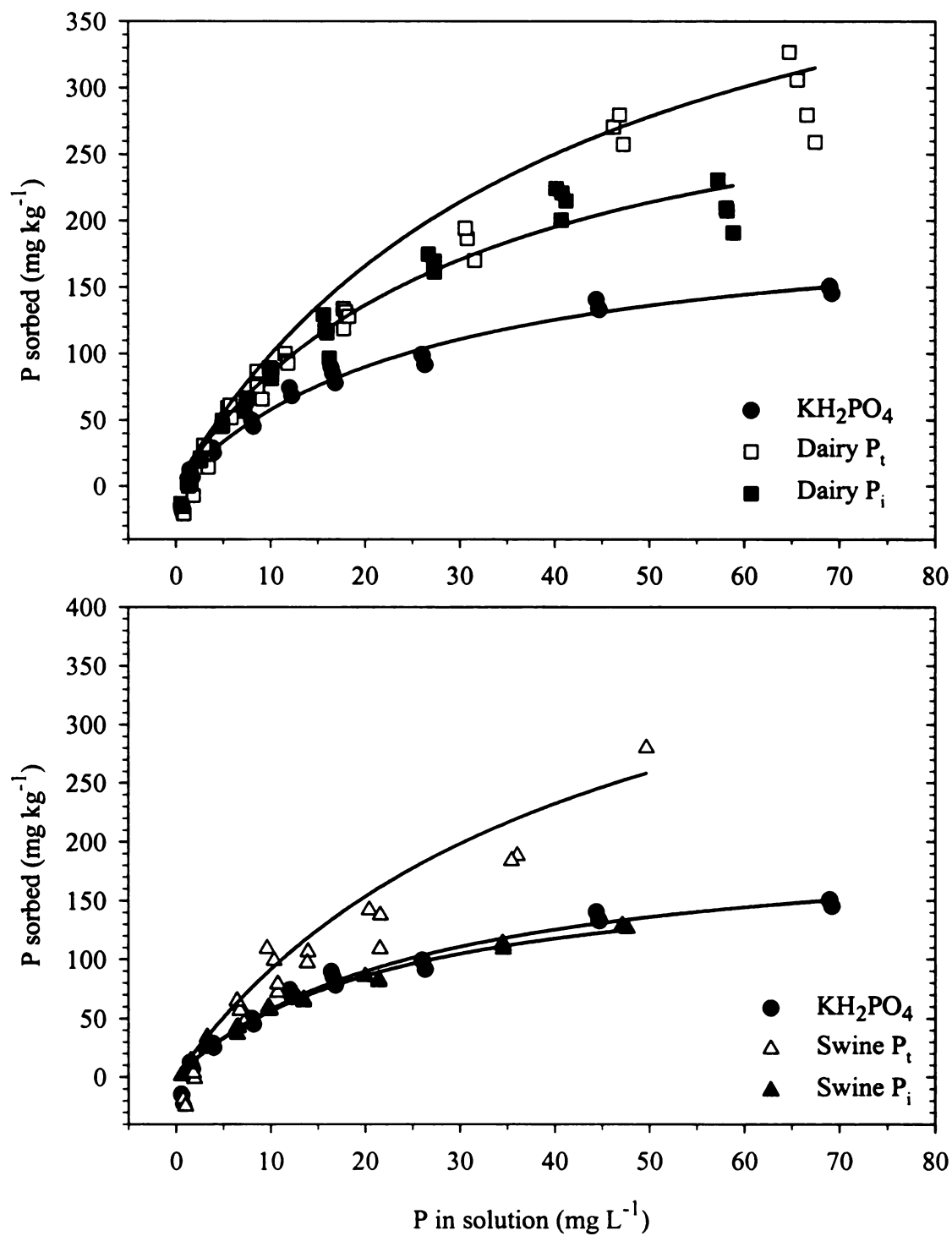


Figure 2.3. Inorganic P (P_i) and total P (P_t) sorption isotherms for Colwood 2 soil.

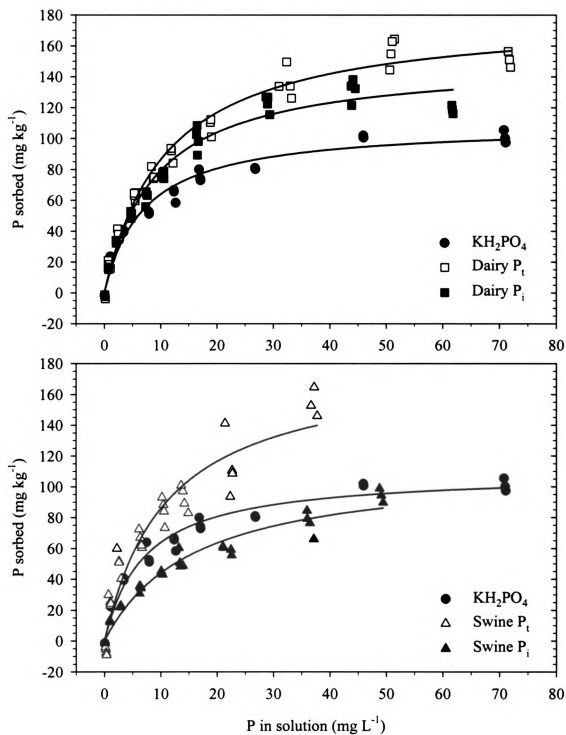


Figure 2.4. Inorganic P (P_i) and total P (P_t) sorption isotherms for Oshtemo soil.

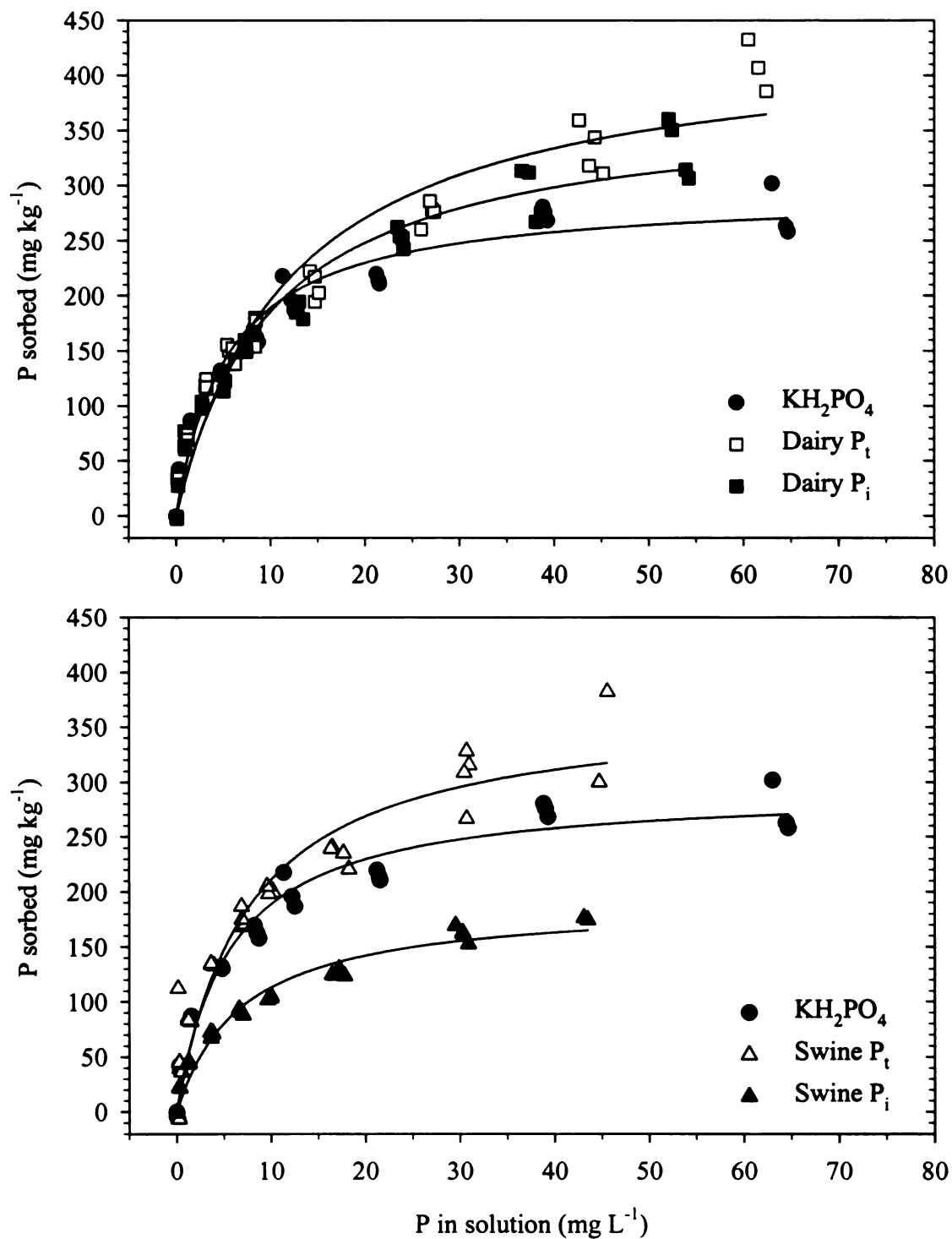


Figure 2.5. Inorganic P (P_i) and total P (P_t) sorption isotherms for Parkhill soil.

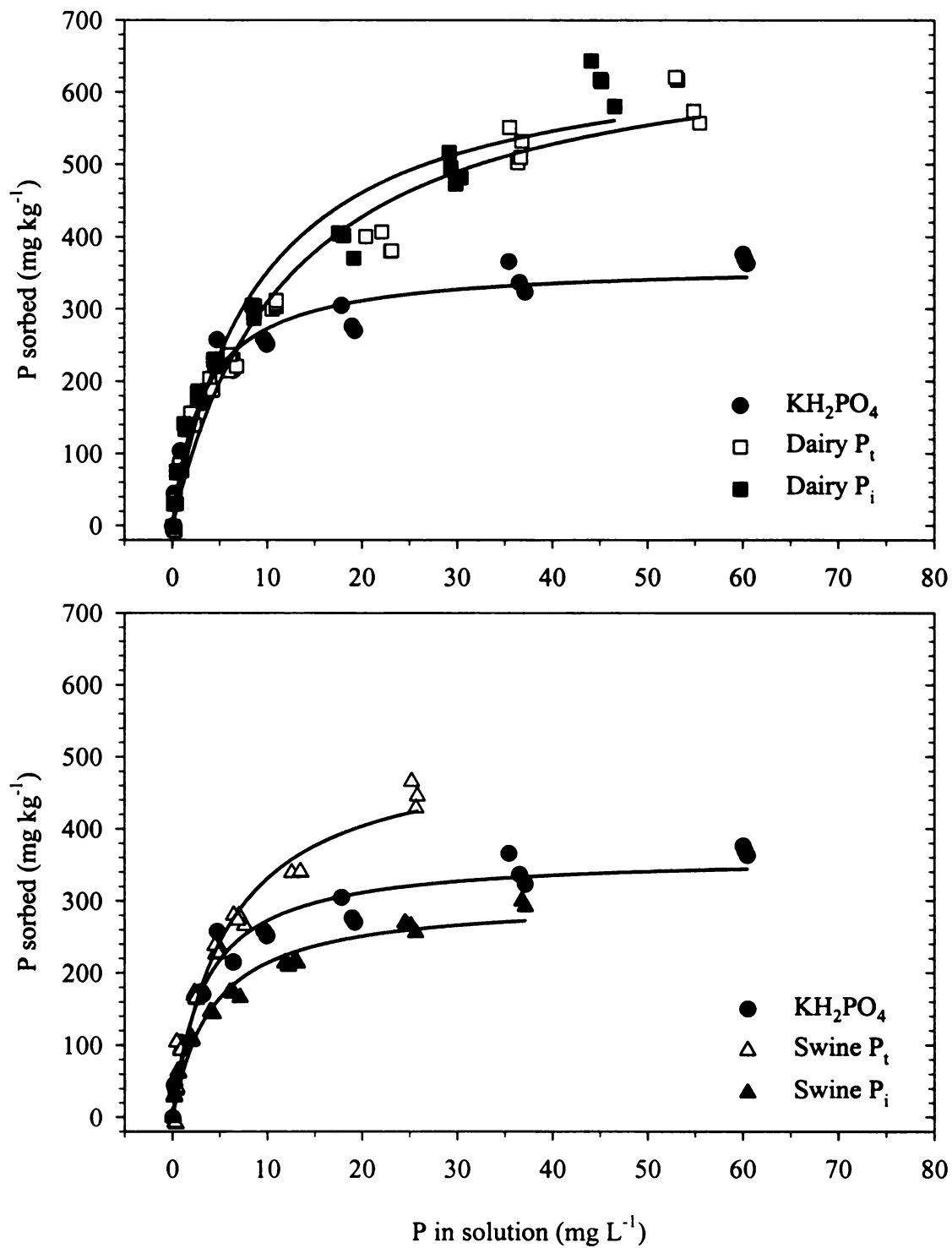


Figure 2.6. Inorganic P (P_i) and total P (P_t) sorption isotherms for Spinks soil.

For Capac, Colwood 2, Oshtemo, and Parkhill soils, P_i sorption capacity was significantly ($\alpha=0.05$) greater than P_i sorption capacity for dairy slurry. While for the Colwood 1 and Spinks soils, P_i and P_i sorption capacities for dairy slurry were not significantly different. P_i sorption capacity of swine slurry was significantly greater than P_i sorption capacity of swine slurry for all soils.

As hypothesized by others, the reduction in P_i sorption capacity observed by swine slurry compared to KH_2PO_4 may be due to preferential blocking of retention sites or displacement of sorbed P by anions of organic acids (Swenson et al., 1949; Kafkafi et al., 1998). The reduction in sorption capacity observed may also be caused by the competition of the P_o portions of the slurry with P_i for binding sites on the soil surfaces (Anderson et al., 1974).

One hypothesis for the increase in sorption capacity observed by dairy slurry compared to KH_2PO_4 is that new sorption sites were created by the dissolution of Fe and Al from soil surfaces by low molecular weight organic acids. This hypothesis is supported by the measured desorption of Fe and Al in equilibrated solutions (Appendix E and F, Table 2.5). The difference between P_i sorbed from dairy slurry and KH_2PO_4 were moderately correlated to desorbed Fe ($r = -0.42$ to -0.64) for all soils except Capac and Colwood 1 soils. The difference between P_i sorbed from dairy slurry and KH_2PO_4 were moderately to strongly correlated to desorbed Al ($r = -0.44$ to -0.72) for all soils except Capac and Colwood 1 soils (Table 2.5). However, the difference between P_i sorption from swine slurry and KH_2PO_4 was not significantly correlated to Fe or Al for any soil with the exception of a moderate correlation to desorbed Al for Capac soil

($r = 0.43$) only. These results support the theory of creation of new P sorption sites caused by the dissolution of Fe and Al from soil surfaces by dairy slurry; likely allowing newly exposed Fe and Al on soil surfaces to sorb P. In addition, desorbed Fe and Al may

Table 2.5. Correlation of desorbed Fe or Al to the difference between inorganic P (P_i) sorption capacity from each slurry and KH_2PO_4 .

P Source	Soil	----- Fe -----		----- Al -----	
		R	<i>P</i> value	<i>r</i>	<i>P</i> value
Dairy	Capac	-0.29	0.0937	-0.44	0.0078
	Colwood 1	-0.28	0.1042	-0.48	0.0041
	Colwood 2	-0.58	0.0002	-0.70	<0.0001
	Oshtemo	-0.42	0.0117	-0.57	0.0003
	Parkhill	-0.46	0.0009	-0.46	0.0086
	Spinks	-0.64	<0.0001	-0.72	<0.0001
Swine	Capac	0.27	0.1502	0.43	0.0206
	Colwood 1	0.03	0.8673	0.27	0.1291
	Colwood 2	0.35	0.0637	0.20	0.2880
	Oshtemo	0.06	0.7380	0.13	0.4825
	Parkhill	0.001	0.9954	0.04	0.8331
	Spinks	0.25	0.1795	0.15	0.4180

be forming complexes with the added organic matter from the dairy slurry possibly forming new P binding sites. It is also possible that P is binding to desorbed Fe and Al and is being considered sorbed to soil. Even though swine slurry, like dairy slurry, causes dissolution of Fe and Al in some soils, there is no significant correlation between desorbed Fe and Al with the differences in P_i sorption. Approximately two times more dairy slurry is needed, compared to swine slurry, to obtain the same P concentration in solution. Addition of twice of much dairy slurry may have resulted in much greater concentrations of organic acids in each solution compared to swine slurry may have

caused greater desorbed Fe and Al and subsequent concentrations of P sorbed to desorbed Fe and Al.

The large magnitude of difference between P_i and P_t sorption capacities for swine slurry is likely caused by the greater selectivity for the sorption of P_o from swine slurry. Thus, a correlation between desorbed Fe or Al and the difference between P_t sorption capacity from swine slurry and KH_2PO_4 would mean that a large difference between P_i and P_t sorption capacity was caused by the formation of P_o and Fe or Al complexes. The difference between P_t sorption capacity from swine slurry and KH_2PO_4 was, in general, not significantly correlated to desorbed Fe and Al from the soil surfaces; meaning that P_o complexes with Fe or Al are likely not being formed (Table 2.6). The difference in P_t sorption capacity for dairy slurry was not correlated to desorption of Fe and Al.

Table 2.6. Correlation of desorbed Fe or Al and difference between total P (P_t) sorption capacity from each slurry and KH_2PO_4 .

P Source	Soil	----- Fe -----		----- Al -----	
		r	P value	r	P value
Dairy	Capac	0.32	0.0761	0.36	0.0427
	Colwood 1	-0.05	0.7875	0.01	0.9443
	Colwood 2	-0.04	0.8457	-0.01	0.9616
	Oshtemo	0.18	0.3162	0.22	0.2234
	Parkhill	-0.17	0.3572	-0.13	0.4704
	Spinks	-0.27	0.1122	-0.19	0.2768
Swine	Capac	-0.26	0.1764	-0.29	0.1221
	Colwood 1	-0.05	0.7700	-0.03	0.8611
	Colwood 2	-0.49	0.0207	-0.31	0.1627
	Oshtemo	-0.03	0.8850	-0.002	0.9927
	Parkhill	0.16	0.4159	0.07	0.7250
	Spinks	-0.10	0.6094	-0.05	0.7920

Phosphorus Sorption Strength

P_i sorption strength (k) of the dairy slurry was significantly ($\alpha=0.05$) less than KH_2PO_4 for Colwood 1 and Spinks soils (Table 2.4). For all other soils, P_i sorption strength of dairy slurry was not significantly different than KH_2PO_4 . P_i sorption strength of swine slurry was significantly less than KH_2PO_4 for Capac and Oshtemo soils. For all other soils, P_i sorption strength of swine slurry and KH_2PO_4 were not different. P_i sorption strength of dairy slurry was not significantly different than swine slurry for Capac, Colwood 2, and Parkhill soils. P_i sorption strength of dairy slurry was significantly less than swine slurry for Colwood 1 and Spinks soils but was significantly greater for Oshtemo soil.

For all soils, P_i sorption strength of dairy slurry was significantly less than the sorption strength of KH_2PO_4 . P_i sorption strength of the swine slurry for Colwood 2, Parkhill, and Spinks soils was significantly less than sorption strength of KH_2PO_4 . For Capac, Colwood 1, and Oshtemo soils, P_i sorption strength of swine slurry was not significantly different than KH_2PO_4 . For Capac, Colwood 1, and Spinks soils, P_i sorption strength was significantly less for dairy slurry compared to swine slurry, but was not significantly different than swine slurry for all other soils.

For all soils, P_i sorption strength was not significantly different than P_i sorption strength of swine slurry. P_i sorption strength was significantly greater than P_i sorption strength of dairy slurry for Capac, Colwood 1, Colwood 2, and Oshtemo soils. For Parkhill and Spinks soils, P_i and P_i sorption strengths of dairy slurry are not significantly different.

Overall, P_i sorption strength of the manure slurries was less than KH_2PO_4 . However, this trend was not always significant. P_t sorption strength of dairy slurry was significantly less than KH_2PO_4 . P_t sorption strength for swine slurry was generally less than KH_2PO_4 ; however, similar to P_i sorption strength, for some soils P_t sorption strength of swine slurry was not significantly different than KH_2PO_4 .

In general, the P_i and P_t sorption strength for slurry of either species was less than KH_2PO_4 . Sorption strength as measured by the Langmuir equation is the average of low and high strength sites (Holford et al., 1997). Thus the observed reduction in P_t sorption strength may be due to the P_o portion of the manure slurries binding to soils, likely at lower sorption strength sites. This may occur because P_t is the sum of P_i and P_o and for the mean sorption strength of P_t to be less than P_i , the sorption strength of P_o would have to be less than P_i . Reduced P_i and P_t sorption strength observed in this experiment for dairy slurry is hypothesized to be caused by: i) the low binding strength of the newly created sites on enlarged organic matter-Fe surface complexes as suggested by Holford et al. (1997) or ii) the low sorption strength associated with the newly created sites on the soil surface by the dissolution of Fe and Al by organic acids. Reduced P_i and P_t sorption strength observed for swine slurry compared to KH_2PO_4 is hypothesized to be due to the competition of organic acids for P sorption sites possibly binding to the high strength sites leaving the lower sorption strength sites for P_i and P_o binding.

Organic Phosphorus Sorption

Comparisons of P_o sorption capacity and strength between P sources, for a given soil, could not be made because the P_o sorption isotherms did not fit the Langmuir equation. Generally, P_o sorption for swine slurry is greater than P_o sorption for dairy

slurry for all soils (Figure 2.7, 2.8, and 2.9). Therefore, these soils have a greater selectivity for P_o from swine slurry as compared to dairy slurry. This trend would be expected because the P_i sorption capacity for swine slurry was less compared to the P_i sorption capacity of dairy slurry, whereas the P_i sorption capacities from swine slurry and dairy slurry were similar. The greater selectivity for P_o from the swine slurry may be the reason for the low sorption of P_i likely because of competition for P binding sites (Anderson et al., 1974).

Conclusions

Dairy slurry and swine slurry, when used as the P source in sorption solutions, impacted P_i sorption capacity differently as compared the sorption capacity of KH_2PO_4 , where dairy slurry resulted in P_i sorption capacities greater than KH_2PO_4 and swine slurry resulted in P_i sorption capacities less than KH_2PO_4 . Dairy slurry and swine slurry, when used as the P source, had a similar impact on P_i sorption capacity as compared to when KH_2PO_4 as the P source. P_i and P_i sorption strength was generally reduced for both dairy and swine slurries as compared to KH_2PO_4 . Desorption of Fe and Al was correlated to the difference in P_i sorption between dairy slurry and KH_2PO_4 but was not correlated to differences for swine slurry and KH_2PO_4 . The differences in influence on sorption characteristics observed by the two manure slurries is likely due to the differences in type and concentration of organic acids for the two sources. However, organic acids were not determined for these sources in this experiment.

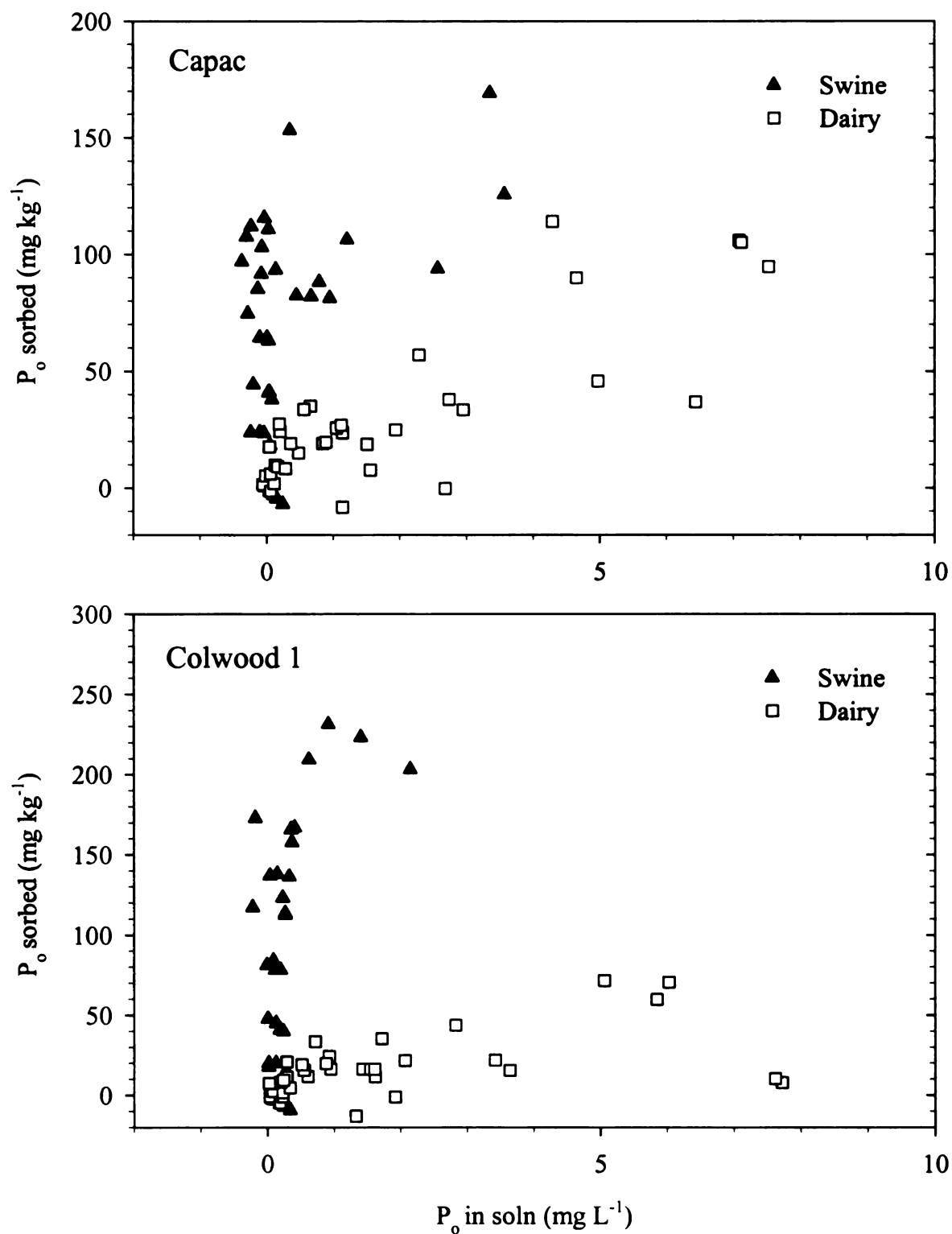


Figure 2.7. Organic P (P_o) sorption isotherms for Capac and Colwood 1 soils.

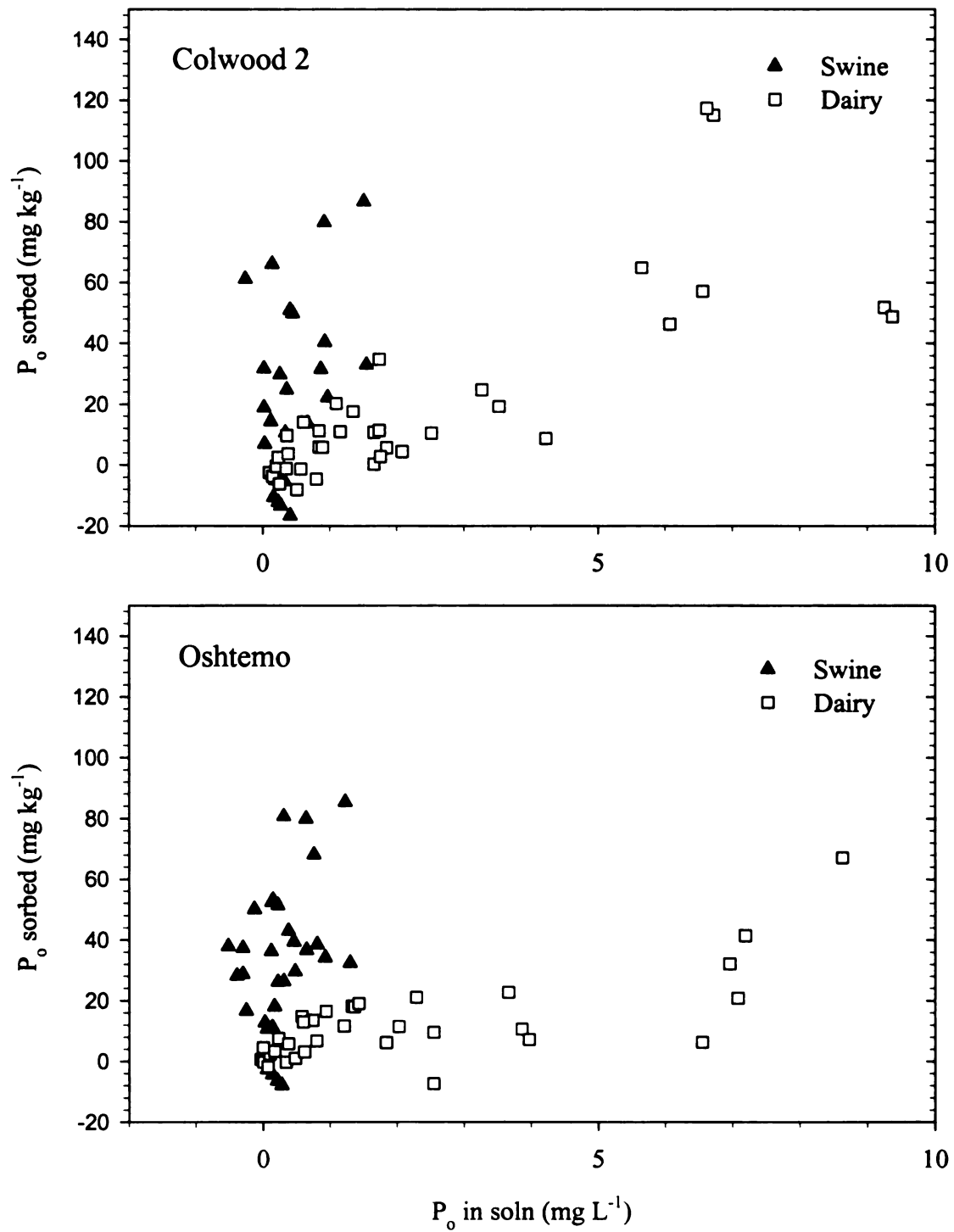


Figure 2.8. Organic P (P_o) sorption isotherms for Colwood 2 and Oshtemo soils.

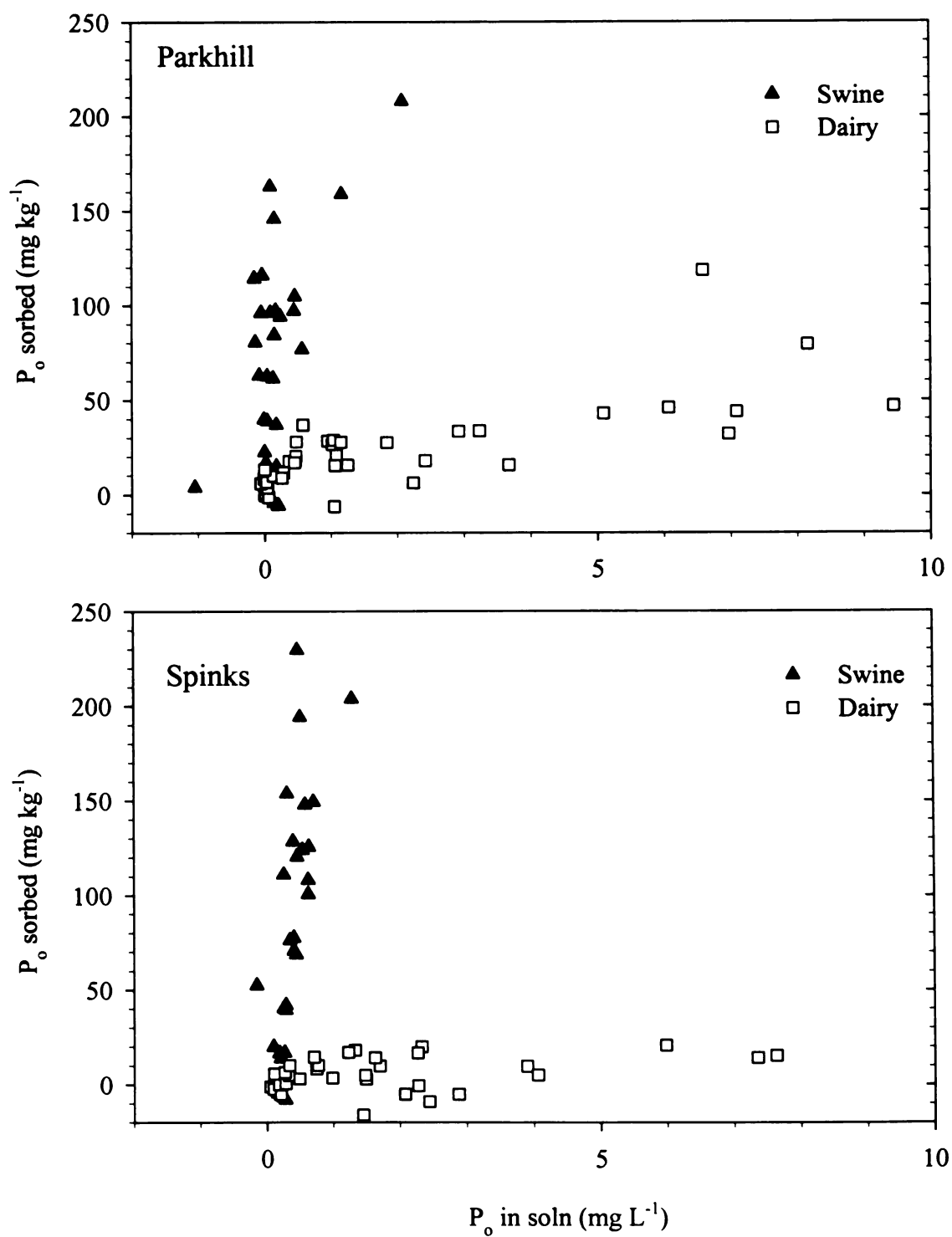


Figure 2.9. Organic P (P_o) sorption isotherms for Parkhill and Spinks soils.

The greater sorption capacity for dairy slurry may suggest it would be less available, as measured by soil test, than fertilizer while the reduction in sorption capacity by swine slurry suggests that it might be more available than fertilizer. Further studies would need to be conducted to determine P availability from these amendments as compared to fertilizer. The results also suggest that dairy and swine slurry have an increased risk for P losses to surface water and leaching potential compared to inorganic fertilizers due to lower sorption strength. Furthermore, dairy slurry having lower sorption strength than swine slurry may have a greater potential to release P into runoff waters. Further investigation is needed to determine the potential for P release to surface water runoff when these manures are applied to soil.

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Chapter 3

Manure application influences on phosphorus sorption and availability of selected Michigan soils

Abstract

A better understanding of the interactions between soil and phosphorus (P) from manure will provide the knowledge needed to develop nutrient management recommendations to reduce environmental risks posed by P loss to water. The objectives of this study were to (i) determine the amount of inorganic P (P_i) that sorbed to soil after application of dairy slurry, swine slurry, or fertilizer (potassium phosphate) and (ii) compare P availability from different P sources. Five soils were incubated with dairy slurry, swine slurry, or fertilizer to create a manure or fertilizer application history. After incubation, sorption isotherms were constructed for each soil and compared to determine the effects of manure application on P sorption characteristics. The relative P availability of manure to increase soil test P compared to fertilizer was calculated.

Overall, incubation with any amendment reduced sorption capacity and strength for at least three of the five soils. The relative availability, as measured by Bray 1-P, of P from dairy slurry was always less than both fertilizer and swine slurry. The relative availability of P from swine slurry was less than fertilizer for three soils and equivalent to fertilizer for two soils. Greater sorption of P_i from dairy slurry leads to lower P availability compared to swine slurry where less P_i sorption of swine slurry leads to similar or less relative P availability. The results from this study suggest that P

availability coefficients for specific manure sources should be developed to provide better guidance when developing nutrient management recommendations.

Introduction

Long term application of manure and/or fertilizer to soil can lead to an increase in available phosphorus (P), as measured by soil tests (Sims, 1993). Application of organic amendments is commonly based on the nitrogen (N) needs of the crop; thus, P is over supplied because manure has a low N:P ratio (Sharpley et al., 1998). Soil test P levels that are greater than agronomic need present an increased environmental risk of P loss to surface waters through agricultural runoff (Sharpley and Sisak, 1997; Sharpley et al., 1998). Increased nutrient loads in surface waters reduce water quality by causing excess algal and plant growth, also known as eutrophication (Sharpley and Menzel, 1987). Elevated soil test P levels may present a greater risk to water quality because of increased potential to transport P to surface and ground water may occur if P sorption properties of a soil change with manure or fertilizer application.

P sorption capacity and strength can change with the application of manure and fertilizer. There surface soils from the Delaware Inland Bay watershed had decreased P sorption capacities and one had an increased P sorption capacity after field application of poultry manure (Mozaffari and Sims, 1994). In this study, P sorption was highly correlated with clay content; in soils with similar clay contents, sorption was greater for untreated areas than manured areas, suggesting manure application has reduced these soils' capacity to retain additional P (Mozaffari and Sims, 1994). In another study, P sorption capacity and strength decreased in soils treated for eight years with poultry, beef, or swine manures as compared to a similar untreated soil (Sharpley et al., 1993). When poultry litter, poultry manure, cattle slurry, sewage sludge, or potassium phosphate (KH_2PO_4) amendments were applied to soil at equivalent rates of total P and incubated

for 20 d P sorption capacity and strength decreased compared to the control (Siddique and Robinson, 2003).

Holford et al. (1997) also found that P sorption capacity and sorption strength were reduced when manures from various animal species, sewage effluent, or superphosphate were applied to soil in the field. The magnitude of the decrease in sorption capacity and strength depended on the amount of manure or effluent applied over time; with increased application rates having a greater reduction in sorption capacity and strength (Holford et al., 1997). Laboski and Lamb (2004) found manure application in a field setting reduced sorption capacity in five of seven Minnesota soils. In these soils, sorption strength was reduced in five soils and unchanged in the other two soils. Both Holford et al. (1997) and Laboski and Lamb (2004) concluded that P sorption strength may have a greater impact on P availability than P sorption capacity. Additionally, they suggest P sorption strength may possibly be the more environmentally important sorption characteristic because reduction in sorption strength results in a greater concentration of P in solution for any given level of P sorbed.

Soils with relatively low P sorption capacity and/or strength may have more available P and present an increased risk for P losses to water bodies. Therefore, it is important to not only understand the effect of manure history on sorption characteristics but also its effect on P availability. Ebeling et al. (2003) found that the availability of P from whole dairy manure, fiber manure, dairy manure (low, medium, and high P), biosolids, and inorganic P (CaHPO_4) was different when amended to soil at equivalent rates of total P (101, 202, and 404 kg total P ha^{-1}) during a 64 wk incubation study.

Bray P-1 soil test levels increased immediately for soils amended with any form of dairy manure, while biosolids and inorganic P showed a more gradual increase of soil test P over time (Ebeling et al., 2003). In contrast, Laboski and Lamb (2003) found that swine slurry increased soil test P more than KH_2PO_4 , when applied at the equivalent rates of total P, after both one and nine months of incubation. Siddique and Robinson (2003) found poultry litter, poultry manure, cattle slurry, sewage sludge, or KH_2PO_4 amendments, applied at equivalent rates of total P, increased $\text{CaCl}_2\text{-P}$ and resin-P. Furthermore, cattle slurry and KH_2PO_4 had a larger influence on $\text{CaCl}_2\text{-P}$, resin-P, and P sorption characteristics, than either the sludge or litters. Siddique and Robinson (2003) speculated that the higher solubility of P in slurry than in KH_2PO_4 was caused by the release of organic acids in the slurry treatment blocking P sorption sites, therefore reducing P sorption capacity.

A better understanding of the impact of manure application on P availability and P sorption characteristics will aid in the development of nutrient management recommendations that reduce potential environmental impact from agriculture. The objectives of this study were to understand the interaction between P availability and P sorption characteristics by (i) determining if and how P sorption characteristics change after manure application and (ii) comparing P availability of dairy slurry, swine slurry, and fertilizer (KH_2PO_4).

Methods and Materials

Soils and Manures

Five surface soils (0-0.15 m) were collected in southern, central Michigan for use in this experiment and are described in Table 3.1. Soils selected had a Bray 1-P soil test level $< 30 \text{ mg P kg}^{-1}$, $\text{pH} < 7$, and varied in soil texture. Prior to experimentation soils were air dried, sieved (2 mm sieve), and thoroughly mixed to ensure homogeneity. Soils were characterized by measuring soil pH, organic matter by loss on ignition, cation-exchange capacity, and Bray 1-P (Brown, 1998). Soil particle size was determined using the hydrometer method (Gee, 1986) (Table 3.1). Water holding capacity of the soils was estimated according to Rawls et al. (1982).

Liquid dairy slurry used in this experiment was collected from a short-term storage pit near a feeding facility. The pit was agitated before sample collection to ensure sample homogeneity. Liquid swine slurry was collected from a slotted floor feeder house at the time of cleaning. Once collected, each species of manure was individually mixed and sieved (2 mm sieve) to accommodate pipetting by removing large residual particles. After collection and sieving, manures were stored in polyethylene containers at 0°C . Manures were characterized by measuring percent moisture, percent solids, total N, total P, soluble salts (K, Ca, Mg, and Na), Al, and Fe (Peters, 2003) (Table 3.2).

Incubation

Four treatments, dairy slurry (100 mg P kg^{-1}), swine slurry (117 mg P kg^{-1}), fertilizer (KH_2PO_4) (100 mg P kg^{-1}), or distilled water (control), were added with a

Table 3.1. Soil characterization and classification.

Soil Series	Classification	pH 1:1 H ₂ O	Organic Matter	Sand	Silt	Clay	CEC [†] cmol _c kg ⁻¹	Bray 1-P mg kg ⁻¹
			----- %			-----		
Colwood 1	Fine-loamy, mixed, active, mesic Typic Endoaquoll	5.6	5.4	42	36	22	16.4	15
Colwood 2	Fine-loamy, mixed, active, mesic Typic Endoaquoll	5.3	6.1	48	40	12	16.9	8
Oshtemo	Coarse loamy, mixed, active, mesic Typic Hapludalf	5.4	2.5	68	23	9	8.3	11
Parkhill	Fine-loamy, mixed, semiactive, nonacid, mesic Mollic Endoaquepts	6.7	5.2	32	39	29	20.1	4
Spinks	Sandy, mixed, mesic Lamellic Hapludalf	4.7	4.5	76	19	5	5.4	14

[†] Cation-exchange capacity.

Table 3.2. Nutrient characterization of dairy and swine manure slurries.

Species	Moisture	Solids	N	P _t [†]	P _i [†]	K	Ca	Mg	Na	Al	Fe
	----- %	-----	-----	-----	-----	-----	mg L ⁻¹	-----	-----	-----	-----
Dairy	95.3	4.7	3271	530	420	2228	1618	539	647	21	57
Swine	94.8	5.2	6542	1254	1102	3810	1078	648	755	53	151

[†] P_t = total phosphorus, P_i = inorganic phosphorus

pipette to 75 g of soil. P sources were incorporated with soil by mixing with a spatula until all soil was moistened and the treatment was evenly distributed. Distilled water was added and incorporated to bring soils to 85% field capacity. Soils were packed to a bulk density of 1200 kg m^{-3} . The liquid volume for the dairy treatment exceeded the water-holding capacity of the Oshtemo soil; thus the total treatment volume was applied over a two day period.

Two replicates of each treatment were incubated at $21.5 \pm 1 \text{ }^{\circ}\text{C}$ for six weeks in covered containers with pinhole openings to allow for aeration while minimizing water loss. Soil moisture was maintained between 80 and 85% field capacity during the duration of the incubation. After incubation soils were air dried and sieved (2 mm sieve).

Laboratory Analysis

Extractable P for all treatments was measured in duplicate by Bray 1-P soil extraction (Frank et al., 1998). Initial P sorption characteristics were measured for each soil prior to incubation. P sorption was measured in duplicate for each replication of the treated incubated soils after incubation.

P sorption was measured using the procedure of Nair et al. (1984) with some modifications. Soils were equilibrated with KH_2PO_4 solutions containing $0\text{-}50 \text{ mg P L}^{-1}$ at a 1:25 (w/v) soil to solution ratio with the addition of 0.14 ml of chloroform for microbial inhibition. Soil solutions were equilibrated for 24 h in an end-over-end shaker. After equilibration, solutions were centrifuged for 10 min at 2350 g and filtered through Whatman No. 1 filter paper (Whatman International Ltd, England). Filtrates were analyzed for inorganic P (P_i) by the ascorbic acid colorimetric method at a wavelength of 882 nm (Frank et al., 1998). Phosphorus sorbed was calculated as the difference between

the amount of P added initially and the amount remaining in the filtrate after equilibration.

Data Analysis

The Langmuir equation is given by:

$$Q = \frac{bkC}{1 + kC} \quad (1)$$

where Q is the amount of P sorbed to the soil (mg P kg^{-1}), C is the amount of P in the solution after equilibration (mg P L^{-1}), b is the sorption maxima (mg P kg^{-1}), and k is the sorption strength (L mg^{-1}). In this experiment, several of the data sets contained data points with negative sorption (desorption) and when nonlinear regression was used the NLIN procedure in SAS (SAS Institute, Inc., 1999) would not converge on the Langmuir equation. Therefore, it was necessary to correct these data sets for the amount of P initially sorbed, Q_o , using the procedure outlined by Laboski and Lamb (2004). When Q_o was not a significant parameter in the regression, it was set to zero. Corrected data sets were fit to equation 1 with nonlinear regression to obtain the estimates and standard errors of the estimates of the b and k parameters. For a given soil, nonlinear regression was used to compare b and k terms of the Langmuir equation between the incubated treatments and non-incubated, non-amended soil. The procedure used was similar to comparing regression coefficients in linear regression (Cook and Weisberg, 1999; Freud and Littell, 2000; Laboski and Lamb, 2004).

The difference between the Bray 1-P soil test of the incubated treated soils and the Bray 1-P soil test of the control soil (no P added) after incubation is the increase in soil test P caused by application of manure or fertilizer. By subtracting the soil test P of the

control soil treatment, a correction was made for P mineralization that may have occurred during the incubation from rewetting dry soil. The increase in soil test P was then divided by the amount of total P applied, giving the increase in soil test P per P applied. This was necessary because the amount of P applied varied with treatment. Comparisons of the impact of the various soil amendments on the increase in soil test P per P applied were made by using analysis of variance (ANOVA) and Fisher's Protected Least Significant Difference (LSD) for mean separation at the $\alpha=0.05$ level.

Relative P availability was calculated by dividing the increase in soil test P per P applied for each manure treatment by the increase in soil test P per P applied for the fertilizer treatment. The relative P availability of a manure treatment compared to fertilizer was considered significantly different than one if the ANOVA for the increase in soil test P per P applied for the two treatments was significantly different (SAS Institute, Inc., 1999). Relative P availability was then interpreted as follows: when the relative availability is equal to one, manure P is equally available as fertilizer P; when the relative availability is significantly greater than one, manure P is more available than fertilizer P; when the relative P availability is significantly less than one, manure P is less available than fertilizer P (Laboski and Lamb, 2003).

Results and Discussion

Phosphorus Sorption Capacity

Sorption capacity was significantly reduced ($\alpha=0.05$) by the application of dairy slurry for Colwood 1, Colwood 2, and Spinks soils, was unchanged for Oshtemo soil, and was significantly increased for Parkhill soil (Table 3.3, Figures 3.1, 3.2, and 3.3).

Table 3.3. Effect of manure and fertilizer application on soil sorption capacity (*b*) and sorption strength (*k*) as estimated by the Langmuir equation.

Soil ID	Incubation Treatment	Total P applied	----- Langmuir Parameters -----			
			<i>b</i>	<i>k</i>	Q_o^{\S}	R ²
		mg kg ⁻¹	mg kg ⁻¹	L mg ⁻¹	mg kg ⁻¹	
Colwood 1	PRE [†]	0	475a [‡]	0.217a	--	0.98
	Dairy	100	411b	0.126b	--	0.98
	Fertilizer	100	410b	0.112b	--	0.98
	Swine	117	389b	0.113b	--	0.99
Colwood 2	PRE	0	178a	0.121a	21.04	0.97
	Dairy	100	143b	0.094b	47.09	0.98
	Fertilizer	100	149b	0.095b	71.05	0.96
	Swine	117	161ab	0.070b	61.29	0.94
Oshtemo	PRE	0	106a	0.231a	--	0.96
	Dairy	100	101ab	0.210a	13.13	0.97
	Fertilizer	100	92b	0.102b	--	0.96
	Swine	117	95b	0.222a	--	0.96
Parkhill	PRE	0	329a	0.200a	--	0.96
	Dairy	100	388b	0.186a	--	0.95
	Fertilizer	100	327a	0.162a	--	0.98
	Swine	117	372ab	0.164a	--	0.93
Spinks	PRE	0	370a	0.311a	--	0.97
	Dairy	100	324b	0.176b	--	0.98
	Fertilizer	100	319b	0.121c	--	0.98
	Swine	117	326b	0.161b	--	0.98

[†] Sorption characteristics for non-incubated non-amended soils.

[‡] Within a soil series, rows within a column followed by the same letter are not significantly different ($\alpha=0.05$).

[§] Q_o is an approximation of the amount of P sorbed to the soil prior to any experimentation. Q_o was used to correct the data sets such that the NLIN procedure (SAS Institute, Inc., 1999) would converge on the Langmuir equation (Laboski and Lamb, 2004).

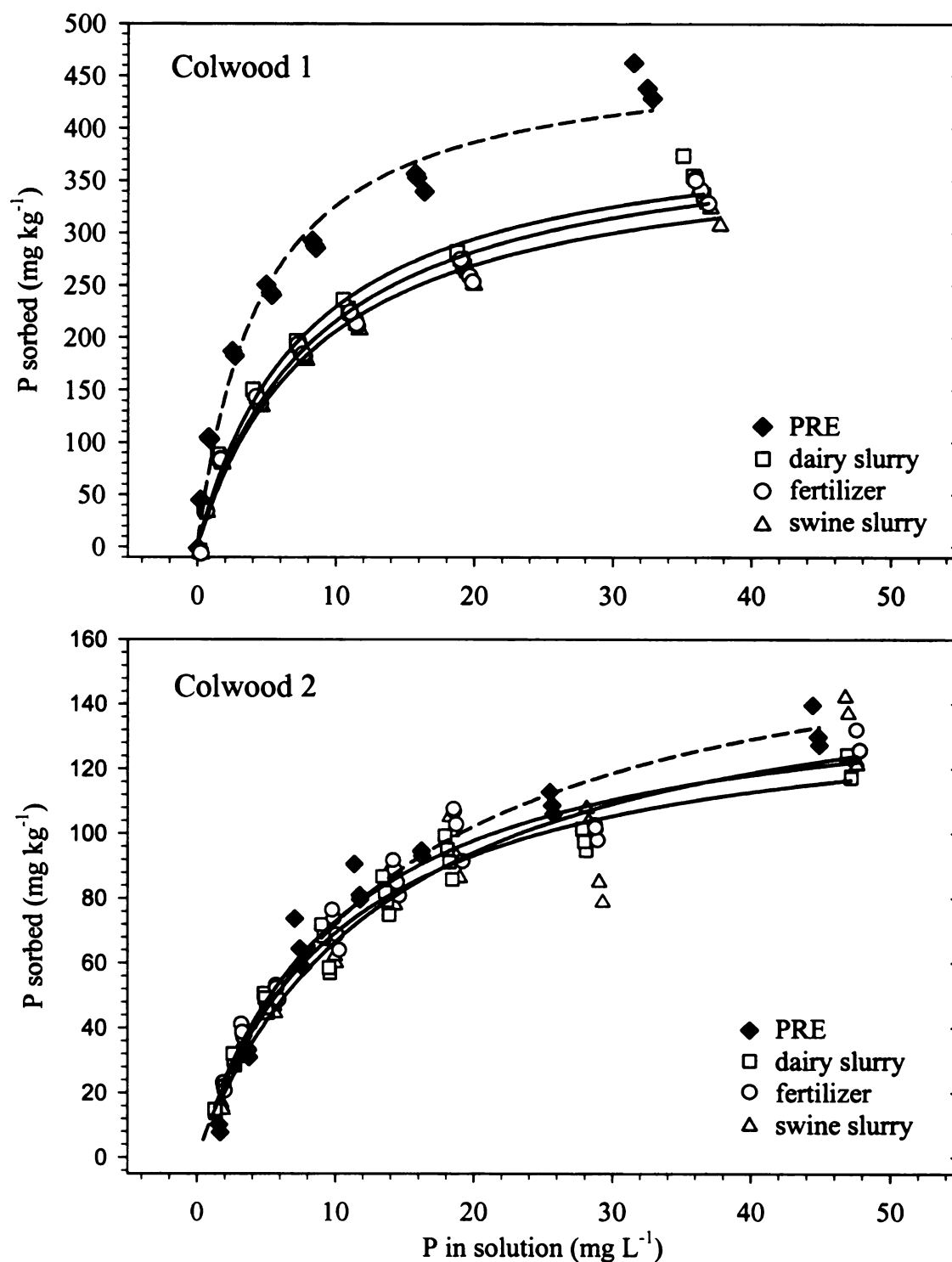


Figure 3.1. Sorption isotherms for Colwood 1 and Colwood 2 soils for non-incubated, non-amended (PRE) and amended incubation treatments.

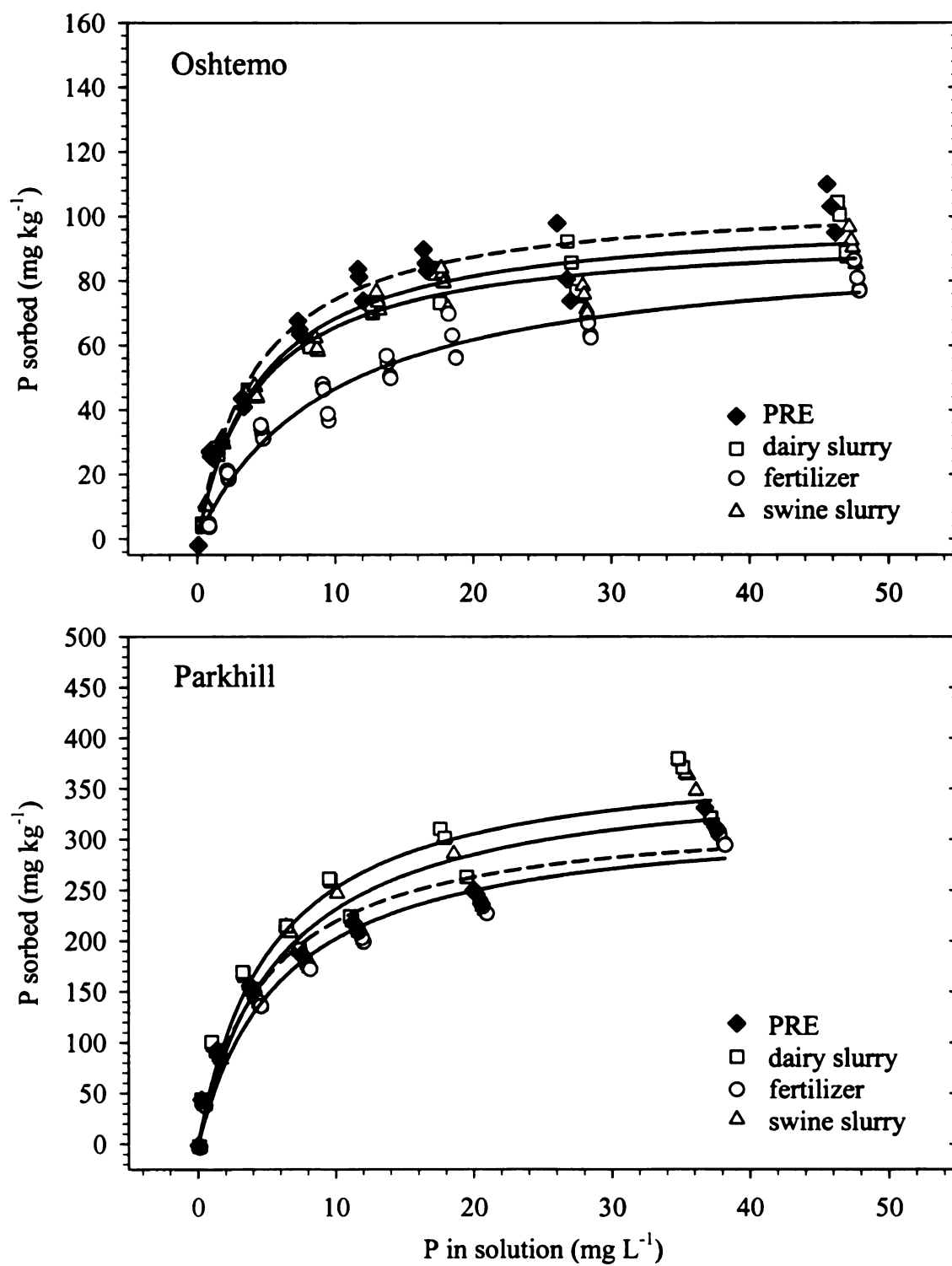


Figure 3.2. Sorption isotherms for Oshtemo and Parkhill soils for non-incubated, non-amended (PRE) and amended incubation treatments.

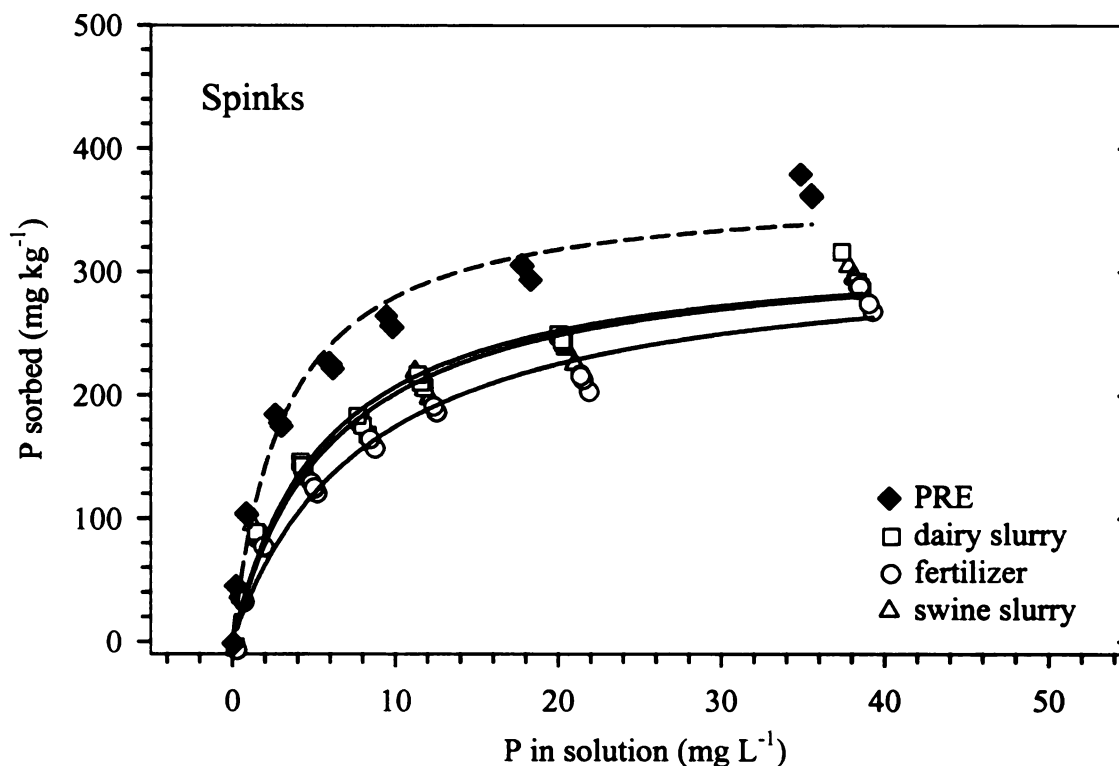


Figure 3.3. Sorption isotherms for Spinks soil for non-incubated, non-amended (PRE) and amended incubation treatments.

Application of swine slurry significantly reduced sorption capacity in the Colwood 1, Oshtemo and Spinks soils, but did not change sorption capacity for Colwood 2 and Parkhill soils. Sorption capacity was unchanged by fertilizer application to the Parkhill soil but was significantly reduced for all other soils.

Siddique and Robinson (2003) also found significant reduction in sorption capacity with the application of poultry litter, poultry manure, cattle slurry, municipal sewage sludge, or fertilizer at a rate of 100 mg P kg⁻¹ during an incubation study. Field studies have also found a reduction in sorption capacity with manure and fertilizer application (Sharpley et al., 1993; Holford et al., 1997; Laboski and Lamb, 2004). The

reduction in P sorption capacity observed with application of manure slurry may be caused by microbial decomposition of soil organic matter and manure producing organic acids that compete with P for surface binding sites (Swenson et al., 1949; Nagarajah et al., 1970; Kafkafi et al., 1998). The reduction in sorption capacity after application of fertilizer is not well understood but may be caused by desorption of initially bound P. However, this amount of P can theoretically be accounted for by correcting the data set using Q_o . This procedure was used for the Colwood 2 and Oshtemo soils in this experiment. However, sorption capacity for the Colwood 2 soil was still reduced, thus Q_o may not be accounting for the total amount of P initially sorbed. If the amount of P initially sorbed is not accounted for then sorption capacity may be reduced because some binding sites were already occupied.

There are far fewer studies that have reported an increase in sorption capacity with manure application (Mozaffari and Sims, 1994; Sharpley, 1996, Laboski and Lamb, 2004). Explanation of this phenomenon is limited. Laboski and Lamb (2004) found that one of seven soils had increased sorption capacity with manure application history. For this soil they found an increase in extractable Fe and Al compared to an adjacent soil in the same soil mapping unit with no manure history. There may have been more P binding sites in this manured soil; however, greater concentrations of extractable Fe and Al were found in other manured soils which had reduced sorption capacity. In the present study Fe and Al in the soils was not measured, thus these relationships can not be explored at this time.

Phosphorus Sorption Strength

Dairy slurry or swine slurry application significantly reduced ($\alpha=0.05$) sorption strength in the Colwood 1, Colwood 2, and Spinks soils, but did not significantly reduce sorption strength in the Oshtemo and Parkhill soils. Fertilizer application significantly reduced sorption strength in the Colwood 1, Colwood 2, Oshtemo, and Spinks soils, but did not significantly reduced sorption strength in the Parkhill soil.

For a given soil, application of either manure slurry or fertilizer reduced sorption strength compared to the sorption strength of the non-incubated, non-amended soil. This supports other studies that have also found a reduction in sorption strength when manures and fertilizers were applied (Holford et al., 1997; Siddique and Robinson, 2003; Laboski and Lamb, 2004). Holford et al. (1997) suggested that the reduction in sorption strength with manure or effluent application history was likely due to organic anion interactions with sorbing P anions thus, lowering the sorption strength. Additionally, Holford et al. (1997) described sorption strength estimated from the Langmuir equation as an average of the total sorption sites which includes high and low strength binding sites in the soil. Holford et al. (1997) suggests that P initially sorbs to high strength sites followed by low bonding strength sites. Thus, reduced sorption strength with the addition of manure or fertilizer may also be caused by the binding of the applied P to lower strength sites because the high strength sorption sites may already be occupied.

Phosphorus Availability

For Colwood 1, Colwood 2, and Parkhill soils the increase in soil test P per P applied was significantly different ($\alpha=0.05$) between all sources (Figure 3.4). This increase in soil test P per P applied for these soils was greatest for the fertilizer followed by swine slurry and dairy slurry, respectively. For the Oshtemo and Spinks soils, swine

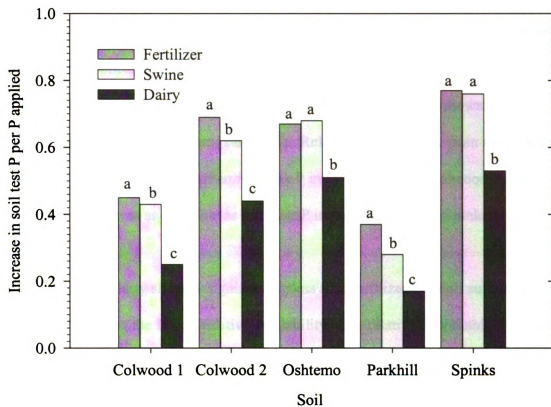


Figure 3.4. Relative increase in Bray 1-P soil test level per P applied during a six week incubation of selected Michigan soils with fertilizer, swine slurry, and dairy slurry. For a given soil, P sources with the same letter are not significantly different ($\alpha=0.05$).

Table 3.4. Relative availability of P from dairy and swine slurries compared to fertilizer.

Soil	Dairy	Swine
Colwood 1	0.56*	0.95*
Colwood 2	0.64*	0.90*
Oshtemo	0.75*	1.01
Parkhill	0.45*	0.74*
Spinks	0.69*	0.99
Mean	0.62	0.92

* Significantly different than fertilizer P ($\alpha=0.05$).

slurry application increased soil test P per P applied as much as fertilizer application whereas, dairy slurry application increased soil test P significantly less than fertilizer or swine slurry application.

Relative P availability from the different P sources were as follows: dairy slurry < swine slurry \leq fertilizer (Table 3.4). Relative P availability from swine slurry was significantly ($\alpha=0.05$) less than fertilizer P in the Colwood 1, Colwood 2, and Parkhill soils but was as available as fertilizer P in the Oshtemo and Spinks soils.

Relative P

availability from dairy slurry is significantly less than fertilizer P for all soils, with Parkhill soil having the lowest relative availability. The relative P availability of dairy slurry is less than the relative P availability of swine slurry for all soils.

The low relative P availability of dairy slurry for the Parkhill soil may be explained by the sorption characteristics of this soil after incubation with the various amendments. This was the only soil where the sorption capacity increased after application of dairy or swine slurries compared to fertilizer. Therefore, the increase in sorption capacity, which was greatest for the dairy slurry amendment likely resulted in a low relative P availability. Dairy slurry application increased sorption capacity more than swine slurry application, though not significant, and had a lower relative P availability compared to swine slurry. It is also important to note that the sorption strength for this soil was unchanged by all amendments compared to the non-incubated, non-amended soil. The low relative P availability of this soil may also be caused by its soil characteristics (Table 3.1). This soil has high clay and organic matter contents and has a low Bray P-1 soil test level. The low relative P availability is likely caused by its

greater sorption capacity and strength or binding affinity for P because of its low P soil test level. In addition, P sorption capacity is generally greater for soils with large concentrations of clay and or organic matter.

Oshtemo and Spinks soils were the only soils where the relative P availability of swine slurry was not significantly different than fertilizer. For these soils the change in sorption capacity between the non-incubated, non-amended soil and the swine slurry or fertilizer amended soil was very similar. For all other soils, the relative P availability of swine slurry was significantly less than fertilizer and the magnitude of the change in sorption capacity upon treatment was much greater than the non-incubated, non-amended soils. Additionally, the Oshtemo soil was the only soil where fertilizer application was the only amendment that significantly reduced sorption strength. However, the sorption strength for Spinks soil was significantly reduced by all amendment treatments. The Oshtemo and Spinks soils were the sandiest (68 % and 76 % respectively) compared to the other soils (32-48 % sand). Therefore, the high relative P availability for these soils may be caused by the low sorptive properties of these soils.

The difference in relative P availability observed for swine and dairy slurries may be explained by the sorption characteristics measured when the slurries or KH_2PO_4 were used as the P source in a sorption experiment (Chapter 2). The P_i sorption capacities for all soils when dairy slurry, swine slurry, and KH_2PO_4 were used as the P source decreased in the following order: dairy slurry > KH_2PO_4 \geq swine slurry; with the magnitude of the change in P_i sorption capacity between dairy slurry and KH_2PO_4 being larger than the change in P_i sorption between swine slurry and KH_2PO_4 . Therefore, dairy slurry having a greater P_i sorption capacity than KH_2PO_4 , when used as the P source,

likely would have a lower relative P availability whereas, swine slurry having a reduced or equivalent P_i sorption capacity compared to KH_2PO_4 likely would have a lower or more similar relative P availability.

The P_i sorption strength is less, however not always significant, for the dairy and swine slurries compared to KH_2PO_4 when used as the P source during the sorption experiment. Additionally, dairy slurry had a lower, however not always significant, P_i sorption strength than swine slurry for all soils except Colwood 2 and Oshtemo. This smaller P_i sorption strength observed when dairy slurry was the P source compared to swine slurry may suggest that dairy slurry would be more available than swine slurry. However, this is not what was shown in the present experiment. These findings do not concur with the conclusions made by Holford et al. (1997) and Laboski and Lamb (2004) that sorption strength may influence P availability more than sorption capacity when manure and fertilizer were applied to soils in a field setting. P sorption capacity was much greater when dairy slurry was used as the P source in sorption experiments compared to swine or KH_2PO_4 . Thus, in the present study it is likely that the increase in sorption capacity and reduction in sorption strength interact to affect P availability.

Dairy slurry had a mean relative P availability of 0.62 (62 %) and P_i was 79 % of P_i . The mean relative P availability of swine slurry was 0.92 (92 %) and P_i was 88 % of P_i . Thus, the relative P availability for a given slurry may be similar to but is not equivalent to percent P_i . If percent P_i was used to estimate relative P availability, then P availability would be overestimated for dairy slurry and underestimated for swine slurry based on the data in this study. Currently, land grant universities in the Midwest are recommending that P from manure be considered 50 % to 100 % available to plants in the

first year of application regardless of animal species (Jacobs, 1995; Busch et al. 1997; Madison et al., 1998; Sutton et al., 2001; Beegle and Curran, 2004). Clearly this one size fits all approach is not appropriate to estimate P availability to crops grown on soils with soil test levels less than or equal to agronomically optimum.

Conclusions

Results of this study show that sorption characteristics can increase, decrease, or remain unchanged with manure or fertilizer application. In this study, at least half the soils had reduced sorption capacity and strength with a manure or fertilizer application.

Dairy slurry application always increased soil test levels less than swine slurry or fertilizer application. These data show that the application of P from swine slurry is more effective in increasing soil test P than dairy slurry over a range of soil textures. These results are supported by other research conducted on these selected Michigan soils where P_i in dairy slurry sorbed to soil more than KH_2PO_4 and P_i in swine slurry sorbed to soil less than KH_2PO_4 . Greater sorption of P_i from dairy slurry leads to lower P availability compared to swine slurry where less P_i sorption of swine slurry leads to similar or less relative P availability.

As shown in this study, the relative availability of P, as measured by Bray 1-P, from swine and dairy slurries, is 92 % and 62 % respectively compared to fertilizer. This suggests that P availability to plants should not be generalized for manure from all animal species. Rather, P availability coefficients for manures from different animal species should be developed to provide better guidance when developing nutrient management

recommendations. Further studies are needed in the field and laboratory to determine P availability from manure to plants in the first through third year after application.

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APPENDICIES

APPENDIX A

Determination of optimum rate of chloroform for microbial suppression in sorption solutions where manure is the P source

Experiment 1

Objective

The standard P sorption procedure proposed by Nair et al. (1984) suggests the use of 20 g L⁻¹ of chloroform for microbial inhibition where KH₂PO₄ is the P source of the sorption solutions. However, a different rate of chloroform would likely be needed when manure is the P source of the sorption solutions because there would be more microbial activity than when KH₂PO₄ is the P source. Therefore, an experiment was designed to determine the rate of chloroform needed to inhibit microbial activity during the 24 h equilibration period when manure is the P source. The objective was to suppress the microorganisms to the point where no change in P_i could be detected between the chloroform treated equilibrated solution and a solution of the same concentration kept at 4 °C until analysis, in which it is assumed no net microbial activity occurs.

Methods and Materials

To determine if a rate of chloroform greater than 20 g L⁻¹, as proposed by Nair et al. (1984), was adequate for microbial suppression when manure is the source of the P for sorption solutions, chloroform (in 0.75% ethanol; guaranteed reagent; EM Science, Gibbstown, NJ) was added at a rate of 0 ml, 0.63 ml, or 1.25 ml to 25 ml of solution where dairy slurry or swine slurry is the P source. Solutions of approximately

75 mg total P L⁻¹ were prepared in 0.1 M KCl at pH 6 for each manure species. The rates of chloroform added are equivalent to 0 g L⁻¹, 36.9 g L⁻¹, and 73.7 g L⁻¹, respectively. Solutions were equilibrated for 24 h at room temperature (approximately 25 °C) in an end-over-end shaker to simulate the conditions under which sorption experiments would take place. After equilibration, solutions were centrifuged for 10 min at 2350 g and filtered through Whatman No. 1 filter paper. Aliquots of the dairy slurry and swine slurry solutions kept at 4 °C were centrifuged and filtered similarly prior to colorimetric analysis. All samples were diluted and analyzed using ascorbic acid color development at a wavelength of 882 nm (Frank et al., 1998). All treatments were run in duplicate.

Results and Discussion

When the 0.63 ml and 1.25 ml rates of chloroform were added to the slurry solutions in 50 ml centrifuge tubes (Corning Inc., Life Sciences; Acton, MA) for a 24 h equilibration period, the tubes became deformed. This is likely due to a reaction of the chloroform with the polypropylene tube. Therefore, these rates can not be used with the previously mentioned tubes for the sorption experiments. Thus, other lower rates of chloroform were investigated for effectiveness of microbial inhibition.

Experiment 2

Objective

The objective of this experiment was to determine if lower rates of chloroform, closer to the rate proposed by Nair et al. (1984), are effective in suppressing microbial activity in a sorption solution of greatest P concentration, where dairy and swine slurry

was the source of P, for the 24 h equilibration period. Effective microbial suppression was determined to be where no change in P_i could be detected between the equilibrated chloroform treated solution and a solution of the same concentration kept at 4 °C, in which it is assumed no net microbial activity occurs.

Methods and Materials

Chloroform was added at a rate of 0 ml, 0.16 ml, or 0.31 ml to 25 ml of solution where dairy slurry or swine slurry was the P source. Solutions of approximately 75 mg total P L⁻¹ were prepared in 0.1 M KCl at pH 6 for each manure P source. The rates of chloroform added are equivalent to 0 g L⁻¹, 9.2 g L⁻¹, and 18.4 g L⁻¹, respectively. Solutions were equilibrated for 24 h at room temperature (approximately 25 °C) in an end-over-end shaker to simulate the conditions under which sorption experiments would take place. After equilibration, solutions were centrifuged for 10 min at 2350 g and filtered through Whatman No. 1 filter paper. Solutions of dairy and swine slurry kept at 4 °C were centrifuged and filtered similarly just prior to colorimetric analysis. All samples were diluted and analyzed using ascorbic acid color development at a wavelength of 882 nm (Frank et al., 1998). All treatments were run in duplicate.

Results and Discussion

The addition of chloroform at a rate of either 0.16 ml or 0.31 ml to 25 ml of solution were not significantly different ($\alpha=0.05$) in suppressing microbial activity for both manure species (Table A.1). For dairy slurry, addition of either 0.16 ml or 0.31 ml of chloroform to 25 ml of solution was significantly better at reducing microbial activity

Table A.1. Comparison of the ability of various rates of chloroform to suppress microbial activity for the 24 h equilibration period.

Rate of Chloroform ml	----- P Source -----	
	Dairy	Swine
	P _i in Solution mg kg ⁻¹	
0 (4 °C)	47.76a [†]	73.01a
0 (25 °C)	44.16b	69.10b
0.16 (25 °C)	46.64c	71.84ab
0.31 (25 °C)	46.70c	69.84ab
LSD ($\alpha=0.05$)	0.841	3.77

[†]Means within a row followed by the same letter are not significantly different as determined by Fisher's Protected Least Significant Difference (LSD) at the $\alpha=0.05$ level.

than 0 ml of chloroform at 25 °C, however, both chloroform rates resulted in significantly lower amounts of P_i in solution than the control at 4 °C. The addition of either 0.16 ml or 0.31 ml of chloroform to 25 ml of solution to the swine slurry solution resulted in statistically similar concentrations of P_i in solution compared to the addition of no chloroform at either 4 °C or 25 °C, however, the concentrations of P_i in solution were significantly different for the two treatments with no chloroform addition (25 °C or 4 °C).

Overall, it appears that the addition of either 0.16 ml of chloroform to 25 ml of solution or 0.31 ml of chloroform to 25 ml of solution will give adequate microbial suppression for swine slurry solutions for the 24 h equilibration period as compared to the control at 4 °C. As for the dairy solution, it appears that these rates of chloroform may not be completely suppressing microbial activity as compared to the control at 4 °C, however, the treatment means are very similar. Thus, significant differences between means may be caused by the small number of replications. Because there was no difference in P_i solution concentrations between these rates of chloroform for both

manure species chloroform at a rate of 0.16 ml of chloroform to 25 ml of solution will further be tested for its effectiveness in the suppression of microbial activity over a range of P solution concentrations where KH_2PO_4 , dairy slurry, or swine slurry is the P source of the sorption solution. It is also important to determine if this rate of chloroform is adequate to suppress microbial activity when solutions are equilibrated with soil.

Experiment 3

Objective

A study was conducted to determine if the rate of 0.16 ml chloroform to 25 ml of solution would be sufficient for microbial suppression with the addition of soil. Degradation of the centrifuge tubes was also a concern after the observed visual deformation with high rates of chloroform. It was hypothesized that P_i would be different, when KH_2PO_4 was used as the P source, without soil, with and without chloroform addition, if any small amount of tube deformation caused changes in the P sorptiveness of the centrifuge tubes.

Methods and Materials

For this experiment three soil variables (no soil, Parkhill, or Spinks) were equilibrated with sorption solutions prepared from each P source (dairy slurry, swine slurry, or KH_2PO_4) at a total P solution concentration of approximately 5 or 75 mg P L⁻¹. Sorption solutions were prepared in 0.1 M KCl at pH 6. Solutions were added at 1:25 (w/v), soil to solution ratio, either with or without the addition of chloroform at a rate of 0.16 ml chloroform to 25 ml of solution. Samples were equilibrated for 24 h at

room temperature (approximately 25 °C) in an end-over-end shaker. After equilibration, samples were centrifuged at 2350 g for 10 min and filtered through Whatman No. 1 filter paper (Whatman International Ltd, England). P_i in solution was measured by ascorbic acid color development at a wavelength of 882 nm (Frank et al., 1998). All treatments were run in triplicate with treatment means given in Table A.2.

Table A.2. Comparison of the efficacy of 0.16 ml of chloroform to 25 ml of solution to suppress microbial growth when added to different soils and P sources.

Treatment [†]	Chloroform rate	
	0 ml	0.16 ml
	P_i in solution (mg L ⁻¹)	
None x D x 5	2.70a [‡]	3.42b
None x S x 5	4.79a	5.59b
None x F x 5	5.15a	5.13a
None x D x 75	48.8a	50.2b
None x S x 75	73.0a	73.6a
None x F x 75	78.4a	78.9a
Parkhill x D x 5	0.257a	0.899b
Parkhill x S x 5	0.758a	1.78b
Parkhill x F x 5	1.43a	1.54b
Parkhill x D x 75	38.2a	37.9a
Parkhill x S x 75	57.7a	59.0a
Parkhill x F x 75	63.3a	62.4a
Spinks x D x 5	0.210a	0.436b
Spinks x S x 5	0.572a	0.875b
Spinks x F x 5	0.700a	0.867b
Spinks x D x 75	27.6a	29.2b
Spinks x S x 75	50.2a	52.0b
Spinks x F x 75	58.7a	57.5a

[†] Treatment = Soil x P source x approximate total P concentration of sorption solution in mg P L⁻¹, where D= dairy slurry, S=swine slurry, and F= KH₂PO₄.

[‡] Means within a row followed by the same letter are not significantly different as determined by Fisher's Protected Least Significant Difference (LSD) at the $\alpha=0.05$ level.

Results and Discussion

When no soil was present where KH_2PO_4 is the P source, at either solution P concentration, P_i in solution was not significantly ($\alpha=0.05$) different with or without chloroform, thus chloroform is not changing the properties of the tube such that P sorption is impacted (Table A.2). For both soils, the addition of chloroform resulted in a significantly ($\alpha=0.05$) greater amount of P_i in solution at the 5 mg P L^{-1} solution concentration where KH_2PO_4 was the P source. For both soils, at the 75 mg P L^{-1} solution concentration, where KH_2PO_4 was the P source, the chloroform treatments were not significantly different ($\alpha=0.05$). This may be because at the higher solution concentrations there is a large enough concentration of P that a change in solution P_i is not noticed when the microbes are suppressed. Whereas at the lower solution concentrations, there is a small enough amount of P that changes in P_i solution concentrations are more noticeable.

For both soils, the addition of chloroform resulted in a significantly ($\alpha=0.05$) greater concentration of P_i in solution at the 5 mg P L^{-1} solution concentration when dairy slurry or swine slurry was the P source. For the Spinks soil, the addition of chloroform resulted in a significantly greater concentration of P_i in solution for the 75 mg P L^{-1} solution concentration when dairy slurry or swine slurry was the P source. In contrast, for the Parkhill soil, the concentration of P_i in solution for the 75 mg P L^{-1} solution concentration was not significantly different with or without the addition of chloroform. The observed difference in microbial suppression between soils at the greater P solution concentration may be due to the differences in microbial communities between the soils.

Overall, the addition of chloroform at a rate of 0.16 ml to 25 ml of solution is sufficient in suppressing the activity of microorganisms.

Conclusions

Based on these results, the addition of chloroform at a rate of 0.16 ml to 25 ml of solution is sufficient in suppressing the activity of microorganisms for the 24 h equilibration period for all P sources. For precautionary purposes centrifuge tubes should only be used once for the batch equilibration process.

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APPENDIX B

Determination of effect of filtration method on inorganic P solution concentration

Objective

The standard P sorption method published by Nair et al. (1984) proposed the use of 0.45 μm membrane filtration of equilibrated, centrifuged samples. However, this method of filtration is costly and time consuming. Therefore, the objective of this study was to determine if there was a difference in inorganic P (P_i) concentration in equilibrated solutions when filtered through 0.45 μm filter units (Millex™ Millipore Corporation, Bedford, MA) or Whatman No. 1 filter paper (Whatman International Ltd, England).

Methods and Materials

Sorption solutions with 0-30 mg P L^{-1} in the form of KH_2PO_4 were prepared in unbuffered 0.01 M CaCl_2 (Nair et al., 1984). Solutions were added to the Oshtemo soil at a 1:25 (w/v) soil to solution ratio. Solutions were equilibrated for 24 h in an end-over-end shaker. After equilibration, solutions were centrifuged for 10 min at 2350 g . Solutions were then filtered using one of the three filter treatments; (i) Whatman No. 1 filter paper, (ii) 0.45 μm syringe filter unit, or (iii) unfiltered (control). All treatments were performed in triplicate. P_i solution concentrations for each treatment were determined by analysis with ascorbic acid color development at a wavelength of 882 nm (Frank et al., 1998). Differences in P_i in solution were determined by Fisher's Protected Least Significant Difference (LSD) at the $\alpha=0.05$ level.

Results and Discussion

For all solution P concentrations, filtration treatments are not significantly ($\alpha=0.05$) different, except for the 30 mg P L⁻¹ solution concentration where Whatman No. 1 filter paper had significantly greater P_i in solution compared to the control and the 0.45 µm syringe filter unit (Table B.1). These results suggest that Whatman No. 1 filter paper is adequate for filtration of equilibrated solutions. Kleinman et al. (2002) found that the effect of filtration method (Whatman No.1 and 0.45 µm membranes) on water extractable P concentrations of manure varied with manure species but that Whatman No. 1 filter paper was adequate. Based on the results from this experiment for sorption solutions using KH₂PO₄ as the P source and the findings of Kleinman et al. (2002) for manure solutions, Whatman No. 1 filter paper was determined to be adequate for filtration of P sorption solutions for all P sources after centrifugation.

Table B.1. Mean inorganic P concentration in solution after 24 h equilibration period with Oshtemo soil followed by one of three filtration treatments.

P solution concentration	----- Filtration Method -----		
	Unfiltered	Whatman No. 1 filter paper [†]	0.45µm syringe filter unit [‡]
0	0.033a [§]	-0.0033a	0.00a
2	0.737a	0.787a	0.793a
4	2.22a	2.21a	2.21a
6	3.59a	3.83a	3.80a
10	7.61a	7.44a	7.37a
16	12.98a	13.13a	12.93a
20	16.92a	17.02a	16.67a
30	26.55a	27.36b	26.36a

[†] Whatman International Ltd, England

[‡] Millex™ Millipore Corporation, Bedford, MA

[§] Means across rows followed by the same letter are not significantly different ($\alpha=0.05$).

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APPENDIX C

Percent removal of inorganic P and total P from manure sorption solutions by centrifugation

Objective

Before inorganic P (P_i) and total P (P_t) analysis for sorption experiments can be conducted, centrifugation of equilibrated solutions is necessary to separate soil particles from solution. However, this poses a potential problem with P_i measurement because the heavier particles in the manure will likely also be removed from solution by centrifugation, resulting in a skewed P_i measurement. Thus, the objective of this study was to determine the percent P_i and P_t removal by centrifugation in manure sorption solutions.

Methods and Materials

Percent removal of P_i and P_t by centrifugation of manure sorption solutions was determined experimentally by comparing the P_i and P_t concentrations in centrifuged and uncentrifuged samples. A representative set of sorption solutions for each manure source were prepared on a P_t basis, using the nutrient content of whole manure, in 0.1 M KCl at pH 6, to obtain P_t concentrations of approximately 0, 5, 20, 50 and 100 mg P_t L⁻¹ for dairy slurry and 0, 5, 15, 30, and 75 mg P_t L⁻¹ for swine slurry. Solutions were added to 50 ml centrifuge tubes (Corning Inc., Life Sciences; Acton, MA) with the addition of 0.16 ml of chloroform (in 0.75% ethanol; guaranteed reagent; EM Science, Gibbstown, NJ) to 25 ml of solution for microbial inhibition. Solutions were equilibrated for 24 h in

an end-over-end shaker at room temperature. After equilibration, one set of five replications of solutions for each species was centrifuged for 10 min at 2350 g while the other set of five replications of solutions was not centrifuged. Aliquots of each solution were reserved for P_i digestion prior to filtration. The remaining portion of each solution was filtered through Whatman No. 1 filter paper for P_i analysis. Filtered solutions, centrifuged and uncentrifuged, were analyzed immediately for P_i by the ascorbic acid colorimetric method at a wavelength of 882 nm (Frank et al., 1998).

Samples were digested according to the persulfate oxidation method of Bender and Wood (2000) with some modifications. Aliquots of equilibrated samples (10 or 5 ml) were diluted to a final volume of 50 ml with distilled water. Diluted samples were then digested with 0.7 g potassium persulfate and 1 ml of 11 *N* H_2SO_4 (Appendix D). Samples were first digested for 1.25 h at approximately 100 °C, and then the hotplate was turned to the maximum setting to increase boiling until the samples were reduced to approximately 10 ml. Cooled samples were diluted with 30 ml of distilled water. After samples were diluted, approximately 5 ml of 2 *M* NaOH was added to adjust the pH of the solution. Solutions were transferred to volumetric flasks and diluted to a final volume of 100 ml. Phosphorus in diluted, digested samples was analyzed by the ascorbic acid colorimetric method at a wavelength of 882 nm (Frank et al., 1998). Digested standards of KH_2PO_4 were used to produce the standard curve for determination of the concentration of P_i in solution.

Data Analysis

Differences in P_i and P_t solution concentrations in centrifuged and uncentrifuged solutions were determined by Fisher's Protected Least Significant Difference (LSD) at $\alpha=0.05$. Percent P_i and P_t removal by centrifugation was determined on an uncentrifuged basis. Variation in P_t removal for different solution concentrations was determined by Fisher's Protected Least Significant Difference (LSD) at $\alpha=0.05$.

Results and Discussion

Centrifugation had no effect on P_i solution concentration for all solution concentrations for swine slurry (Table C.1). Whereas, for dairy slurry the uncentrifuged samples had significantly greater P_i in solution for the 20 and 50 mg P_i L^{-1} solution concentrations than centrifuged samples. All other solution concentrations (0, 5, and 100 mg P_i L^{-1}) for dairy slurry had similar P_i solution concentrations for centrifuged and uncentrifuged samples. All solution concentrations, except 0 mg L^{-1} , for both dairy and swine slurries, had significantly greater P_t in solution for the uncentrifuged samples compared to centrifuged samples (Table C.2).

Centrifugation did not remove P_i differently over range of solutions for either dairy or swine slurries (Table C.3). For dairy slurry, P_t removal was similar for the 20, 50, and 100 mg P_t L^{-1} solutions and was significantly ($\alpha=0.05$) greater for these solutions compared to the 5 mg P_t L^{-1} solution. For swine slurry, P_t removal was similar in the 5, 15, and 30 mg P_t L^{-1} solutions, whereas P_t was removed by centrifugation at a significantly greater percentage for the 75 mg P_t L^{-1} solution as compared these solution concentrations. P_i as a percent of P_t is fairly consistent over the range of P solution

concentrations for centrifuged and uncentrifuged samples for both species (Table C.4).

Thus, there was a general consistency in the composition of P (P_i and P_o) in solution over the range of sorption solutions.

Table C.1. Effect of centrifugation on inorganic P (P_i) solution concentration.

P Source	Solution concentration [†] mg P_i L ⁻¹	----- Mean P_i in solution ----- Uncentrifuged Centrifuged ----- mg L ⁻¹ -----		<i>P</i> value [‡]
Dairy	0	0.02	0.02	0.4714
	5	3.24	3.25	0.8597
	20	13.21	13.06	0.0241
	50	34.16	33.21	0.0398
	100	65.69	65.70	0.1853
Swine	0	0.02	0.03	0.3972
	5	4.20	4.24	0.1248
	15	13.53	13.51	0.7639
	30	25.06	25.54	0.2676
	75	60.93	61.39	0.5844

[†] Approximate total P (P_t) concentration of sorption solutions based on the nutrient content of whole manure.

[‡] Significance for comparison of mean inorganic P (P_i) in solution for uncentrifuged and centrifuged samples.

Table C.2. Effect of centrifugation on total P (P_t) solution concentration.

P Source	Solution concentration [†] mg P_t L ⁻¹	----- Mean P_t in solution -----		<i>P</i> value [‡]
		Uncentrifuged	Centrifuged	
		----- mg L ⁻¹ -----		
Dairy	5	4.47	4.04	0.0295
	20	17.99	15.52	<0.0001
	50	46.57	38.99	0.0001
	100	90.59	76.98	<0.0001
Swine	5	4.66	4.44	0.0004
	15	14.88	14.07	<0.0001
	30	29.35	26.79	<0.0001
	75	74.85	62.09	<0.0001

[†] Approximate total P (P_t) concentration of sorption solutions based on the nutrient content of whole manure.

[‡] Significance for comparison of mean total P (P_t) in solution for uncentrifuged and centrifuged samples.

Table C.3. Percent inorganic P (P_i) and total P (P_t) removal by centrifugation for varying solution concentrations. For a given P source and P component (P_i and P_t), removal is compared over the range of solution concentrations.

P Source	Solution concentration [†] mg P_t L ⁻¹	Mean P_i	Mean P_t
		removal	removal
		%	%
Dairy	5	-0.13	9.8
	20	1.13	13.7
	50	2.74	16.3
	100	0.94	15.0
LSD ($\alpha=0.05$)		NS [‡]	2.14
Swine	5	-0.87	4.6
	15	0.12	5.4
	30	-1.9	8.7
	75	-0.77	17.1
LSD ($\alpha=0.05$)		NS	3.93

[†] Approximate total P (P_t) concentration of sorption solutions based on the nutrient content of whole manure.

[‡] NS=Not significant at $\alpha=0.05$.

Table C.4. Percent inorganic P (P_i) of total P (P_t) for centrifuged and uncentrifuged samples.

P Source	Solution concentration [†]	P_i as a percent of P_t uncentrifuged	P_i as a percent of P_t centrifuged
	mg P_t L ⁻¹	%	%
Dairy	5	72	80
	20	73	85
	50	73	88
	100	73	85
LSD (0.05)		NS [‡]	2.14 [§]
<i>P</i> value		0.7990	<0.0001
Swine	5	90	95
	15	91	96
	30	85	94
	75	81	98
LSD (0.05)		2.30	NS
<i>P</i> value		<0.0001	0.3721

[†] Approximate P_t concentration of sorption solutions based on the nutrient content of whole manure.

[‡] NS= Not significant at $\alpha=0.05$ level.

[§] Means, for a given manure species, within a column were separated using Fisher's Protected Least Significant Difference test ($\alpha=0.05$).

Conclusions

No P_i is removed by centrifugation. Some P_t is removed by centrifugation; however, the percent is similar over most solution concentrations. Removal of P_t from solution is a problem when determining P_t sorption characteristics. However, a method could not be determined to separate the soil particles and not preferentially separate out a portion of the P in the manure. It is unknown if the portion of organic P (P_o) that is removed by centrifugation is reactive in P sorption experiments. It was assumed that similar amounts of P_o are removed by centrifugation after manure is equilibrated with and without soil. Thus, if a similar amount of P_o is not measured in solution before and after

equilibration then it is unnecessary to know the exact amount removed by centrifugation because P sorption is calculated as the difference between the initial and final solution concentrations.

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Appendix D

Determination of the optimum amount of potassium persulfate for complete total P digestion of manure slurry

Objective

Preliminary research showed that 0.5 g potassium persulfate, as proposed by Bender and Wood (2000), was not providing complete digestion of diluted manure solutions. Thus, the objective of this study was to determine the optimum amount of potassium persulfate needed to completely digest diluted solutions of manure and measure total P (P_t) in the manure solutions.

Methods and Materials

To determine P_t recovery, dairy and swine phosphorus (P) sorption solutions of low, moderate, and high P concentration were digested with varying rates of potassium persulfate. Diluted manure solutions were prepared on a P_t basis in 0.1 M KCl at pH 6, to obtain P_t concentrations of approximately 10, 30, and 100 mg P_t L⁻¹. Theoretical P concentrations of the diluted manure solutions were determined based on P content of whole manure which was determined by digestion and analysis of dry ashed samples (Peters, 2003).

Solutions were digested using a persulfate oxidation method with some modifications (Bender and Wood, 2000). The amount of potassium persulfate used varied from 0.5 g to 0.7 g in 0.05 g increments to determine the optimal amount needed.

The temperature and duration of boiling were also adjusted in an attempt to increase recovery. Preliminary results (data not shown) had shown the optimum amount of potassium persulfate needed was 0.7 g when first digesting at a temperature of approximately 100 °C for 1.25 h, and then turning the hotplate to the maximum setting, to increase boiling, until the sample had reduced to approximately 10 ml. The amount of sulfuric acid (1 ml of 11 N H₂SO₄) suggested in the method of Bender and Wood (2000) was sufficient for digestion.

To determine repeatability of this adjusted method, samples were digested in three separate runs using the same sorption solutions as previously mentioned. Sorption solutions were digested in triplicate within each run. P_i solution concentration was determined by the ascorbic acid colorimetric method at a wavelength of 882 nm (Frank et al., 1998).

Results and Conclusions

For P sorption solutions with the greatest P concentrations, recovery was improved when 0.7 g potassium persulfate was used in addition to reducing the amount of sorption solution from 10 ml to 5 ml. The average P_i recovery, over all runs, for dairy and swine slurries was 92% and 98.3%, respectively (Table D.1). The recovery was consistent between runs and was similar at low, moderate and high P solution concentrations for a given manure. The recovery for dairy slurry is a little lower than desired but if P in this slurry can not be digested it is likely not reactive with soil in sorption experiments either. If a similar amount of organic P (P_o) is not digested in initial and equilibrated samples then poor recovery does not affect P sorption results.

Table D.1. Average percent total P (P_t) recovery, of three replications, using 0.7 g potassium persulfate.

P Source	Run	Experimental P conc [†] mg L ⁻¹	Theoretical P conc [‡] mg L ⁻¹	Average Recovery %
Dairy	1	9.27	10	92.7
		27.68	30	92.3
		89.25	100	89.3
	2	9.32	10	93.2
		27.97	30	93.2
		89.32	100	89.3
	3	9.38	10	93.8
		27.86	30	92.9
		91.49	100	91.5
	Average	9.32	10	93.2
		27.8	30	92.8
		90.0	100	90.0
LSD (0.05)				1.02
Swine	1	9.88	10	98.8
		29.19	30	97.3
		73.93	75	98.6
	2	9.83	10	98.3
		28.87	30	96.4
		73.93	75	98.6
	3	9.92	10	99.2
		29.43	30	98.1
		74.44	75	99.2
	Average	9.88	10	98.8
		29.2	30	97.3
		74.1	75	98.8
LSD (0.05)				NS [§]

[†] Average experimental P_t concentration of sorption solutions after digestion using 0.7 g potassium persulfate and one ml of 11 N H_2SO_4 .

[‡]Theoretical P_t concentration of sorption solutions based on the nutrient content of whole manure.

[§] NS= Not significant at $\alpha=0.05$ level.

References

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- Frank, K.D., D. Beegle, J. Denning. 1998. Phosphorus. *In* Recommended Chemical Soil Test Procedures of the North Central Region. North Central Region Research Pub. No. 221 (revised). Missouri Agriculture Experiment Station. SB1001.
- Peters, J.(ed). 2003. Recommended Methods of Manure Analysis. Bulletin A3769, University of Wisconsin Extension. Cooperative Extension Publishing, Madison, WI. I-2/2003.

APPENDIX E

Relationship between Fe and Al in solution and desorbed Fe and Al

The following graphs illustrate the relationship between Fe and Al in solution and Fe and Al desorbed from soil for dairy and swine slurries for each soil. Regression equations and parameters are provided for each relationship when significant. Further details of the data analysis are provided in Chapter 2.

In general, Fe and Al desorbed from soil constituents for both slurries with more desorption in soils equilibrated with dairy slurry compared to swine slurry. Furthermore, the relationship between Al concentrations in solution and desorbed Al were stronger compared to similar relationships for Fe. No apparent desorption of Fe and Al occurs when soils are equilibrated with KH_2PO_4 solutions with a range in P concentrations (Table E.1.).

Table E.1. Mean of four replications Fe and Al solution concentrations after equilibration with soil when KH_2PO_4 was the P source.

Soil	P solution	Mean Al in solution	<i>P</i> value for $H_0: \text{Al} = 0$	Mean Fe in solution	<i>P</i> value for $H_0: \text{Fe} = 0$
	mg L ⁻¹	mg L ⁻¹		mg L ⁻¹	
Capac	0	-0.050	0.6729	0.043	0.7314
	20	0.020	0.9162	0.050	0.8075
	75	0.280	0.1772	0.200	0.2692
Colwood 1	0	0.227	0.0439	0.103	0.5423
	20	0.027	0.8262	-0.197	0.1058
	75	0.470	0.0537	0.250	0.0624
Colwood 2	0	0.183	0.3897	0.027	0.8941
	20	0.177	0.3283	0.020	0.8495
	75	0.397	0.0610	0.217	0.2044
Oshtemo	0	-0.150	0.6381	-0.087	0.6395
	20	0.140	0.0454	-0.090	0.6560
	75	0.010	0.9599	0.013	0.9258
Parkhill	0	-0.387	0.1572	0.067	0.4773
	20	0.103	0.7960	0.040	0.8346
	75	0.210	0.4011	0.327	0.0853
Spinks	0	-0.263	0.6180	-0.243	0.5681
	20	0.240	0.3503	-0.07	0.6868
	75	0.457	0.2135	0.290	0.3414

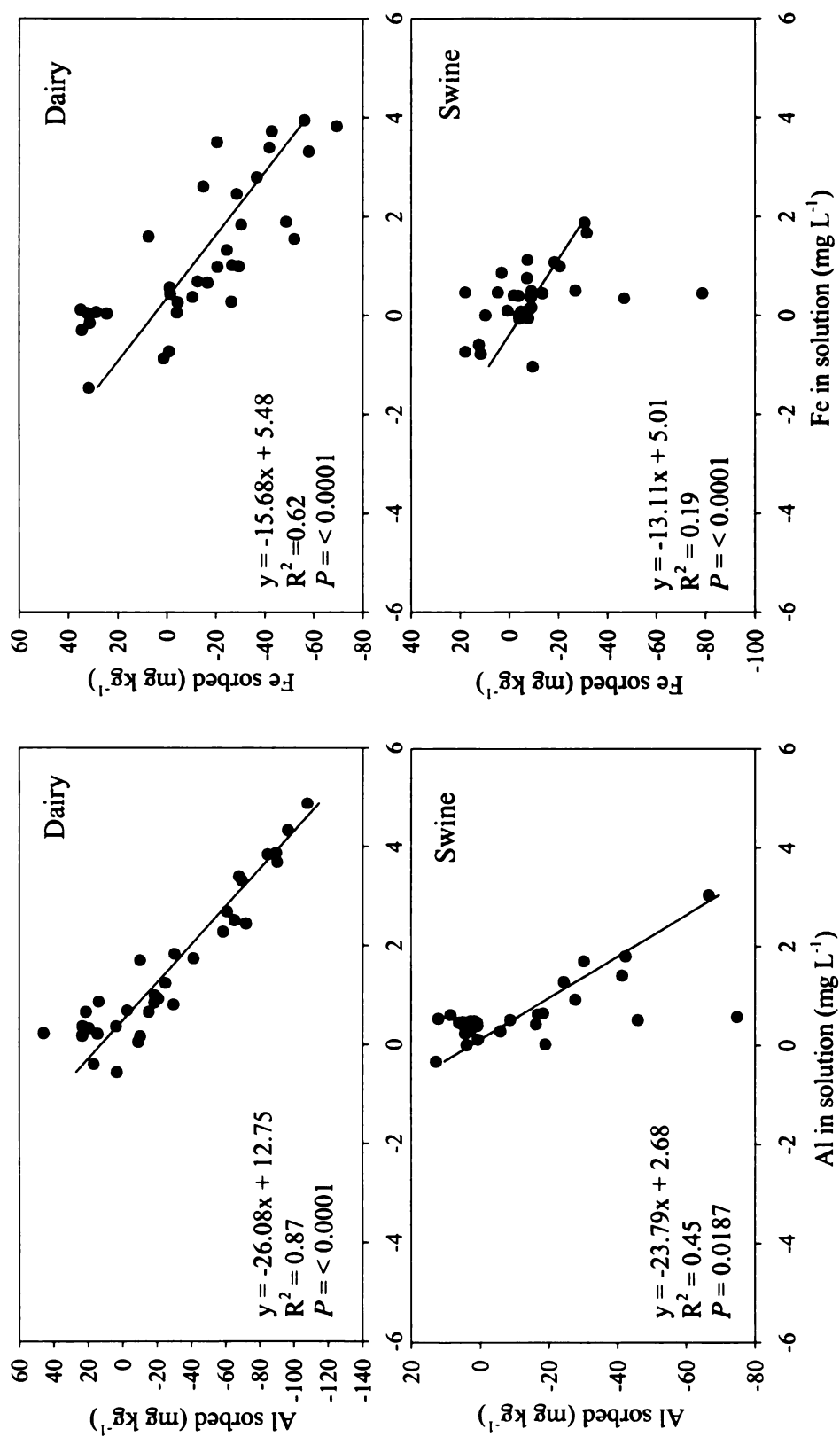


Figure E.1. Relationship between Fe or Al in solution and desorbed Fe and Al for dairy and swine slurries for Capac soil. Regression parameters are provided when significant.

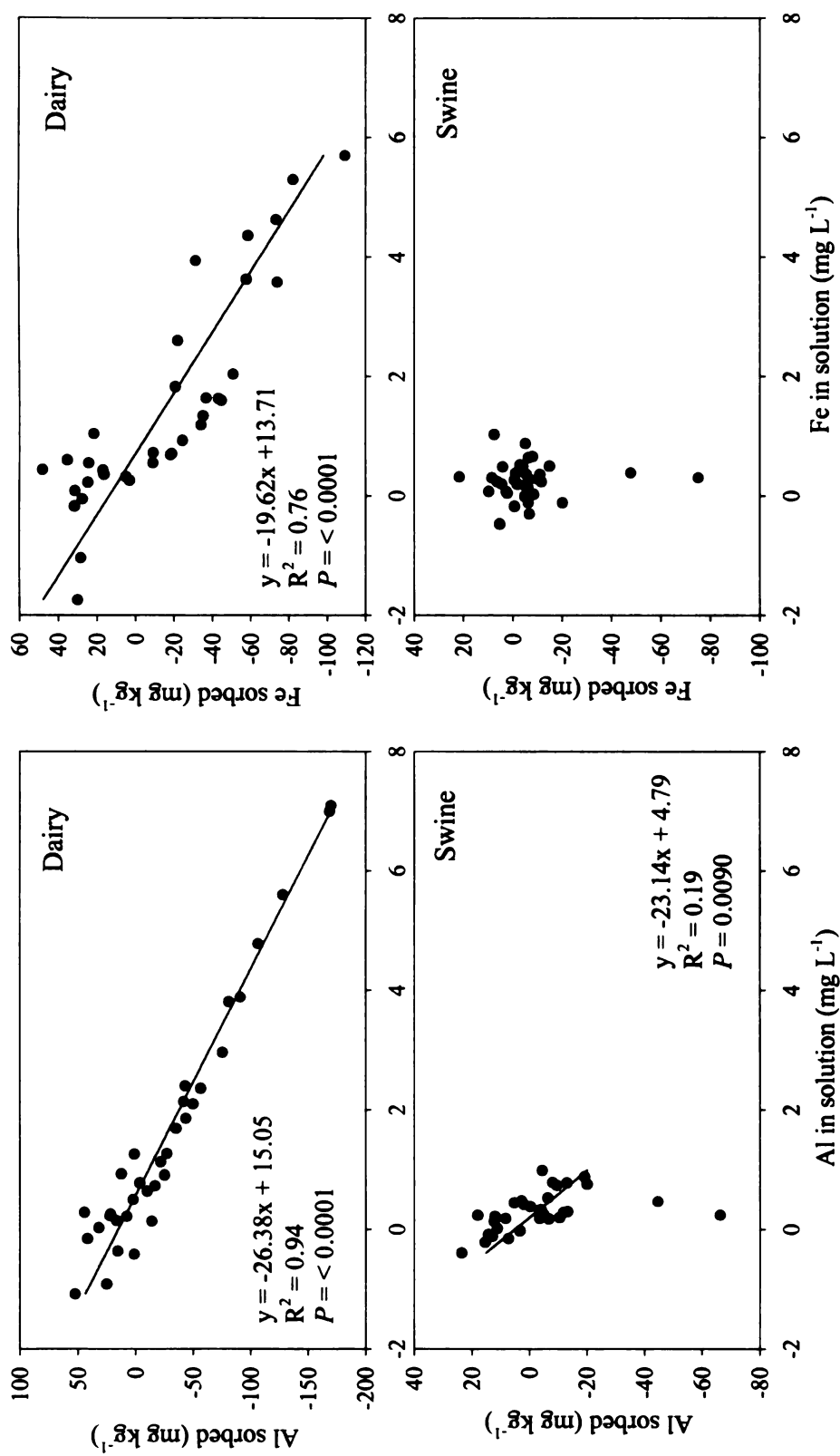


Figure E.2. Relationship between Fe or Al in solution and desorbed Fe and Al for dairy and swine slurries for Colwood 1 soil. Regression parameters are provided when significant.

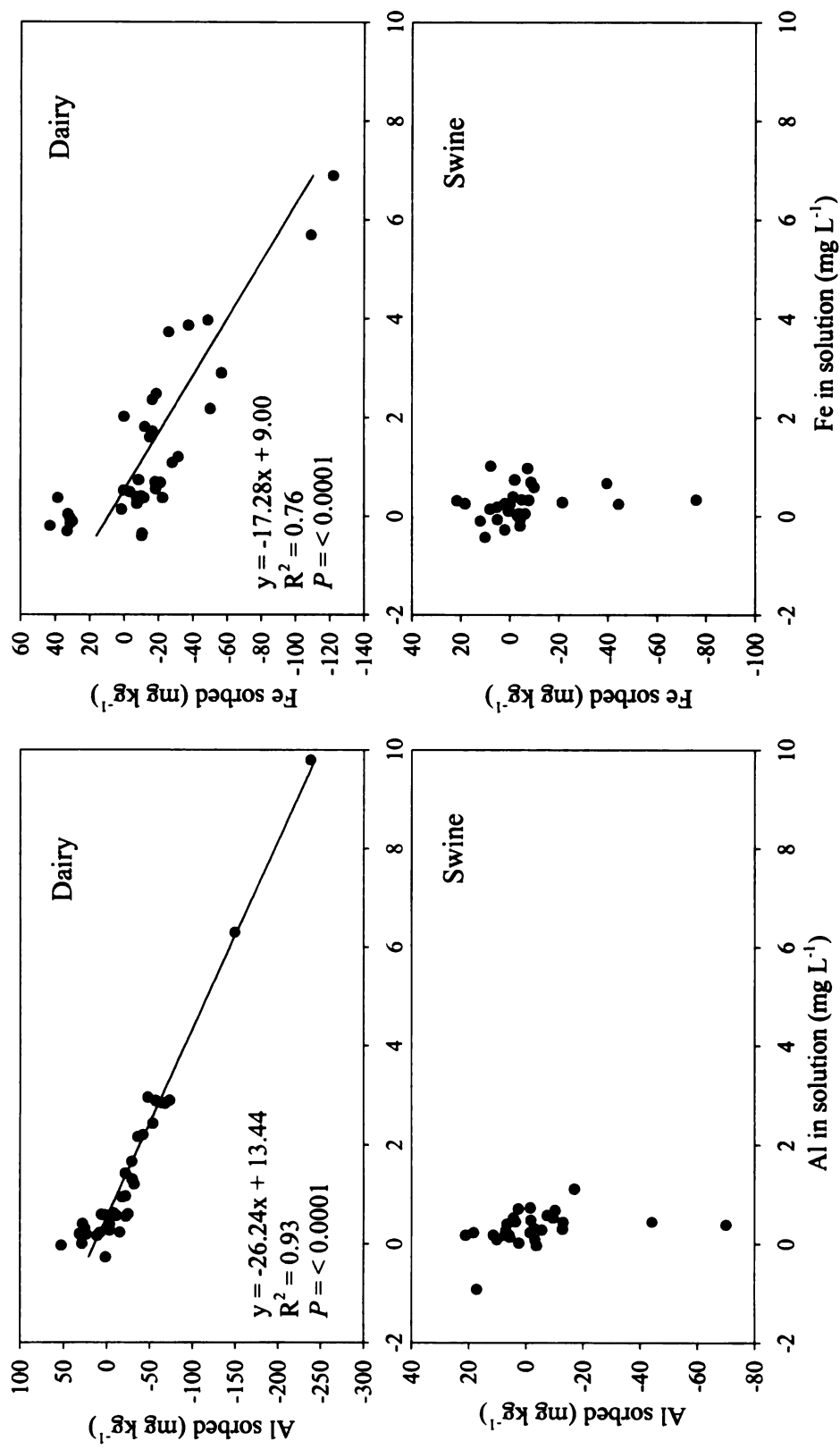


Figure E.3. Regression between Fe or Al in solution and desorbed Fe and Al for dairy and swine slurries for Colwood 2 soil. Regression parameters are provided when significant.

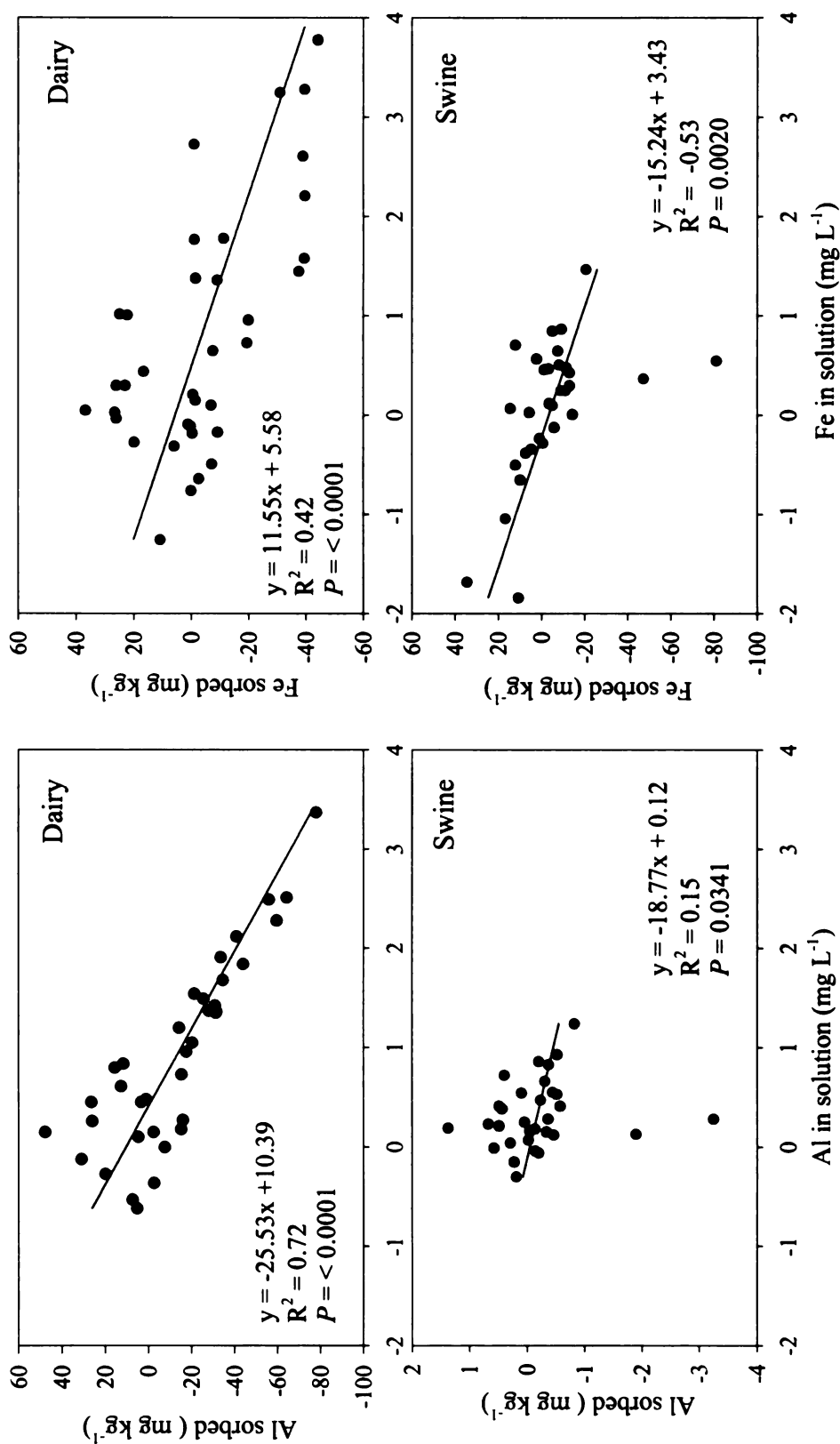


Figure E.4. Relationship between Fe or Al in solution and desorbed Fe and Al for dairy and swine slurries for Oshtemo soil. Regression parameters are provided when significant.

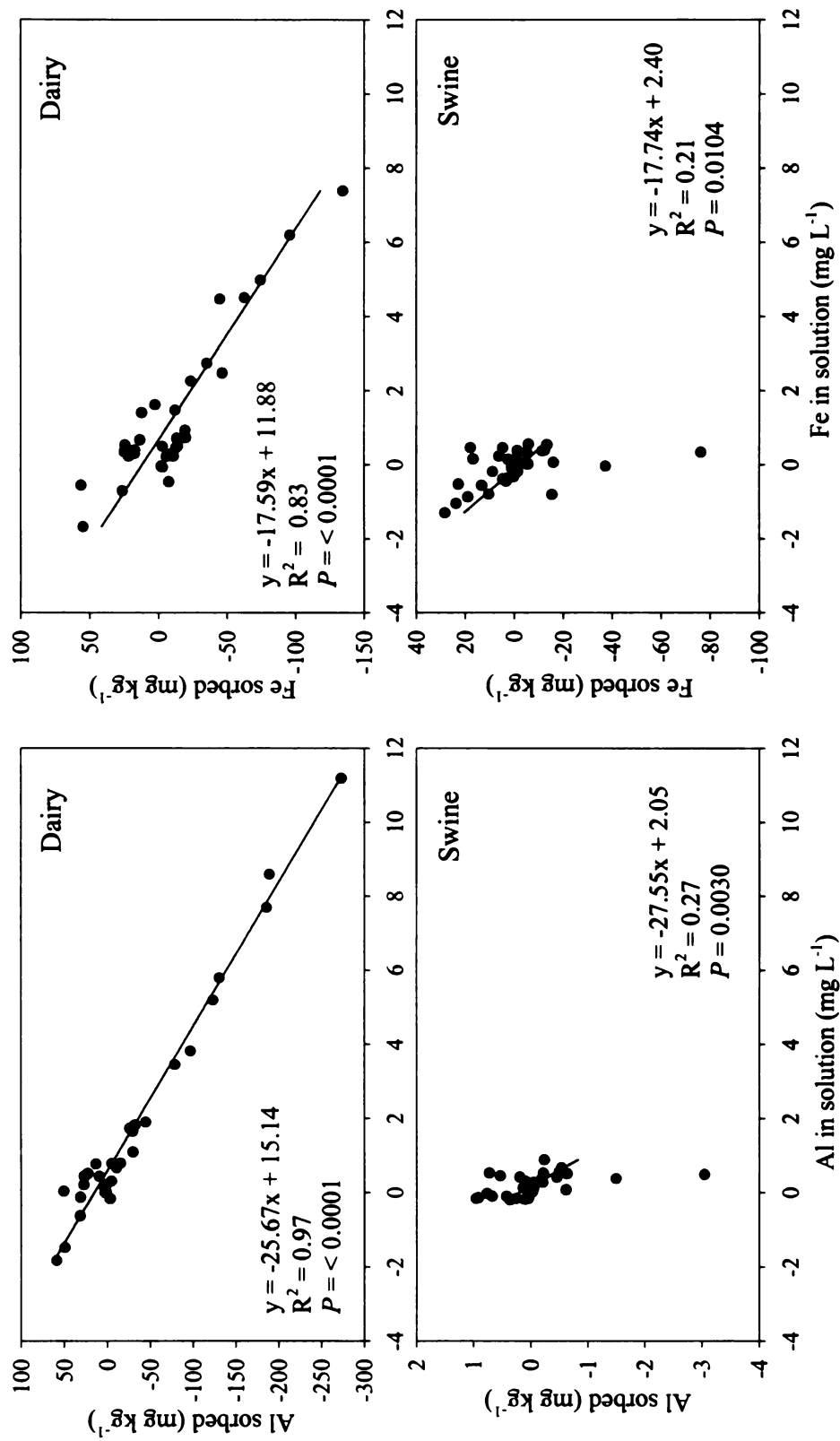


Figure E.5. Relationship between Fe or Al in solution and desorbed Fe and Al for dairy and swine slurries for Parkhill soil. Regression parameters are provided when significant.

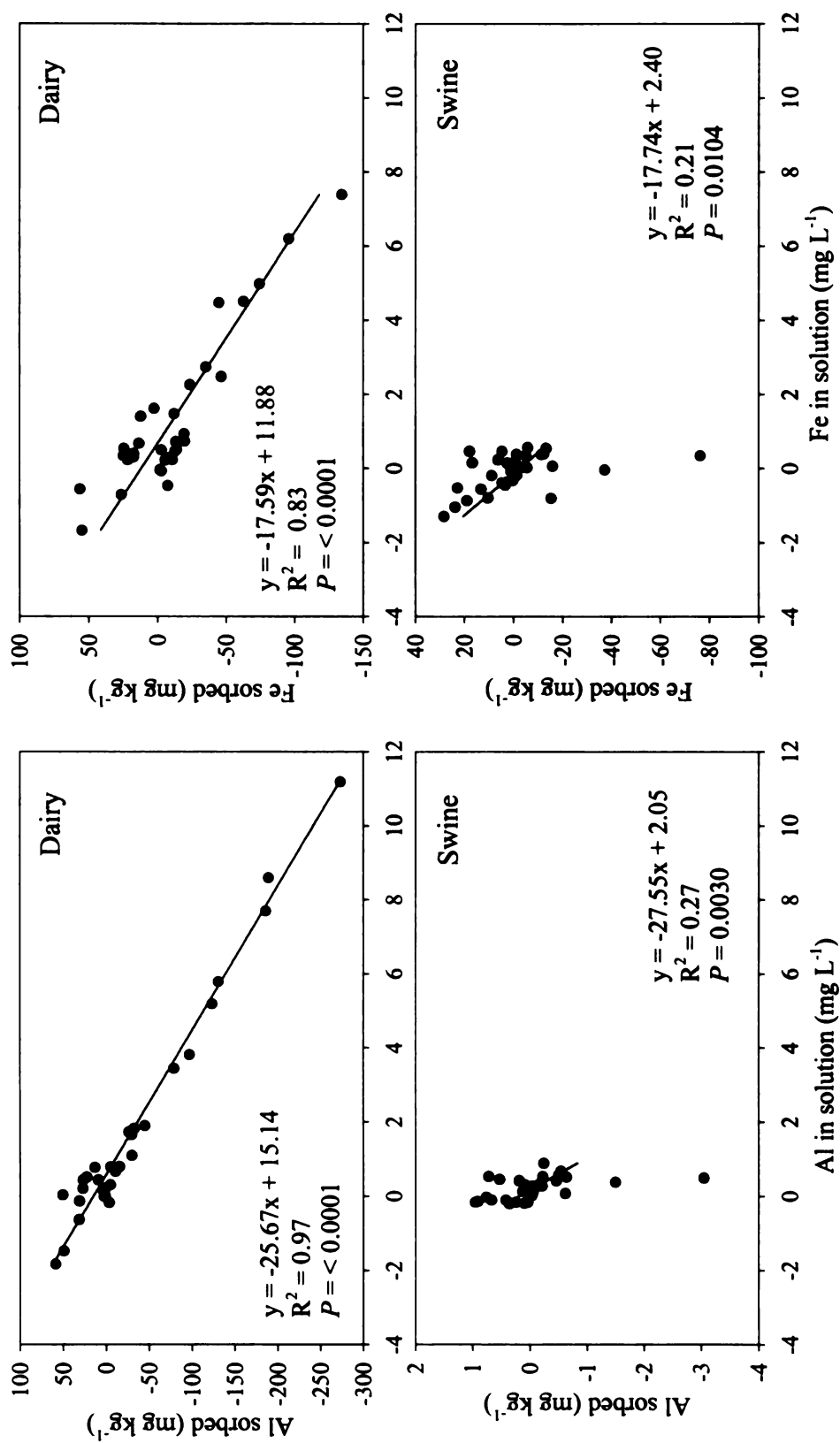


Figure E.6. Relationship between Fe or Al in solution and desorbed Fe and Al for dairy and swine slurries for Spinks soil. Regression parameters are provided when significant.

APPENDIX F

Relationship between desorbed Fe or Al and the difference in inorganic P or total P sorption for slurry and KH_2PO_4 .

The following graphs illustrate the relationship between the difference in P_i sorption capacity between each slurry and KH_2PO_4 . Where the correlation is significant, the correlation coefficient and the level of significance are given for each relationship.

Further details of data analysis are provided in Chapter 2.

In general, the difference between P_i sorbed from dairy slurry and KH_2PO_4 were moderately to strongly correlated to desorbed Fe or Al for all soils except Capac and Colwood 1 soils. Whereas, the difference between P_i sorption from swine slurry and KH_2PO_4 was moderately correlated to desorbed Al for Capac soil ($r = 0.43$) only and was not significantly correlated to desorbed Fe for any of the soils.

In general, the difference between P_t sorbed from dairy slurry and KH_2PO_4 as well as the difference between P_t sorbed from swine slurry and KH_2PO_4 were not significantly correlated to desorbed Fe or Al (Table 2.6).

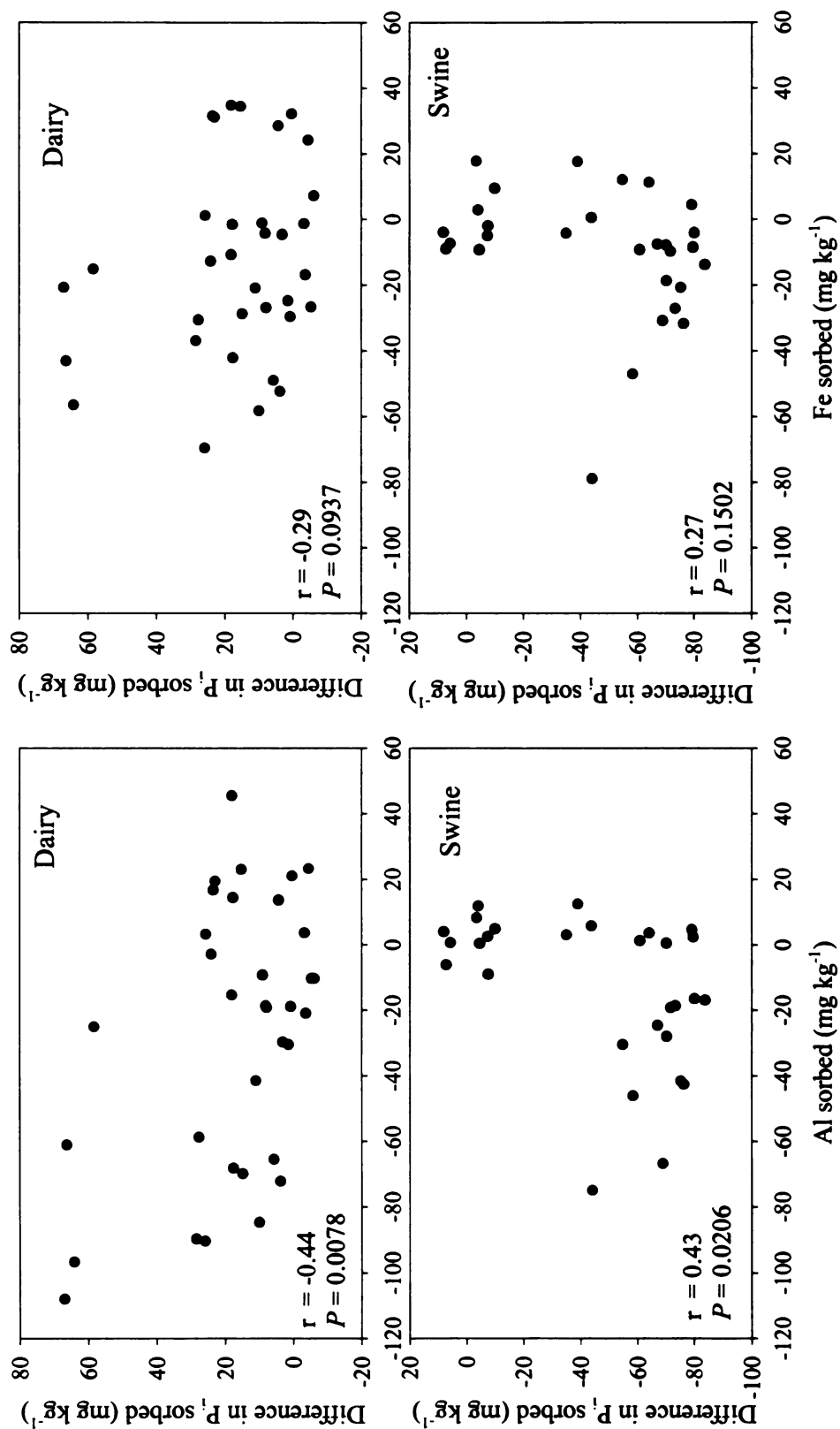


Figure F.1. Correlation of desorbed Fe or Al and the difference in P_i sorption for manure slurries and KH_2PO_4 for Capac soil where r is the correlation coefficient and P is the significance of the correlation.

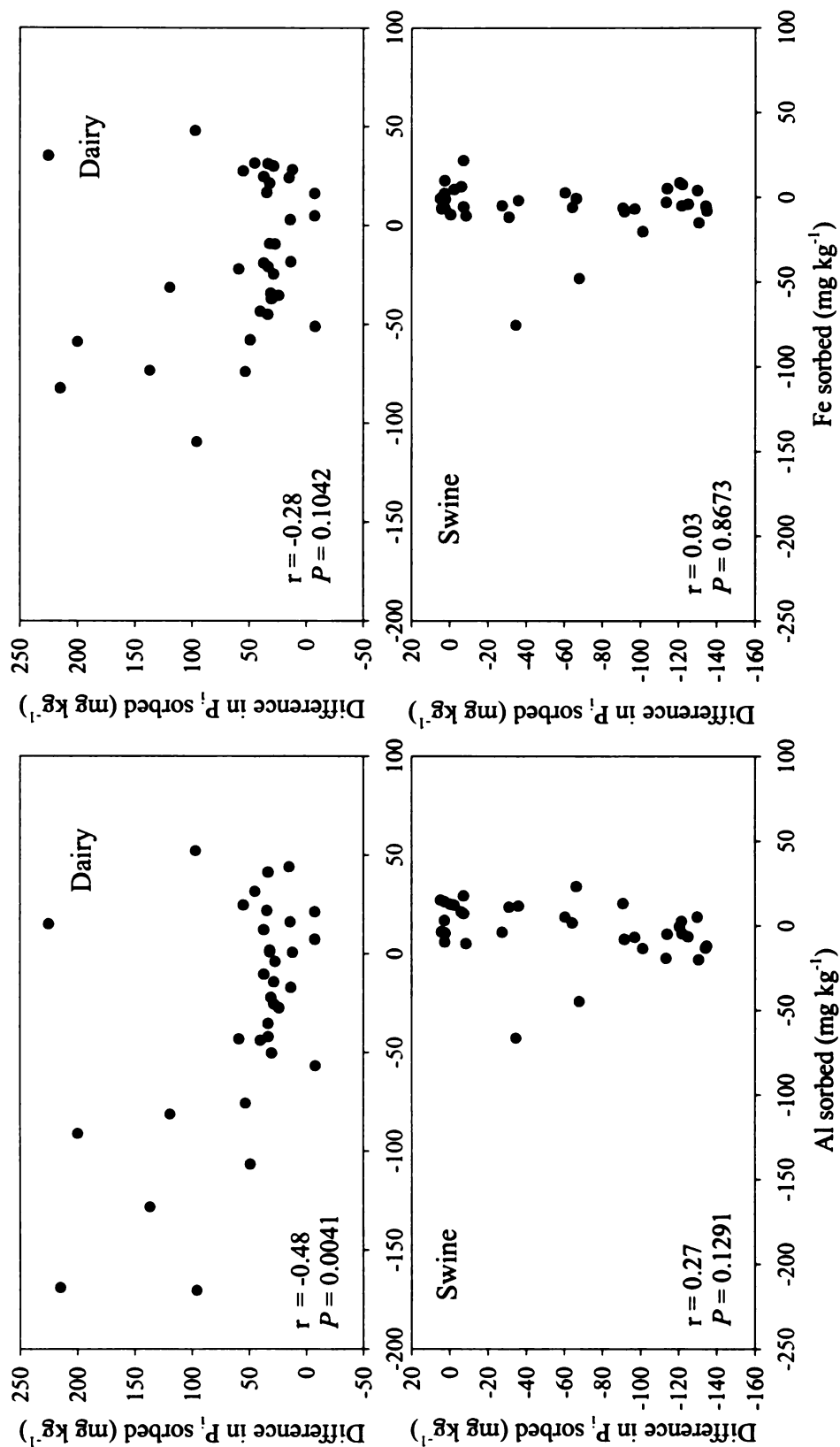


Figure F.2. Correlation of desorbed Fe or Al and the difference in P_i sorption for manure slurries and KH_2PO_4 for Colwood 1 soil where r is the correlation coefficient and P is the significance of the correlation.

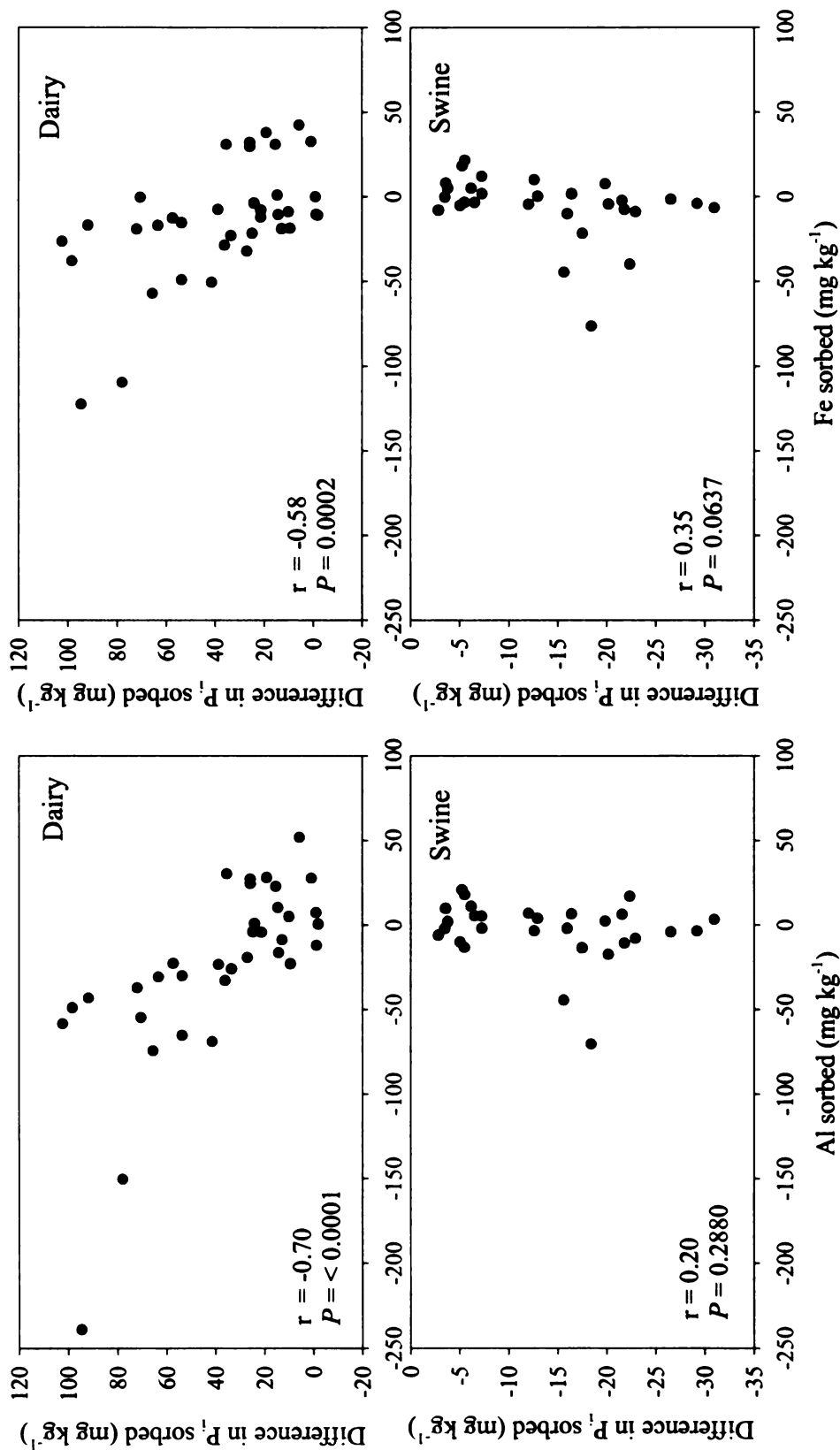


Figure F.3. Correlation of desorbed Fe or Al and the difference in P_i sorption for manure slurries and KH_2PO_4 for Colwood 2 soil where r is the correlation coefficient and P is the significance of the correlation.

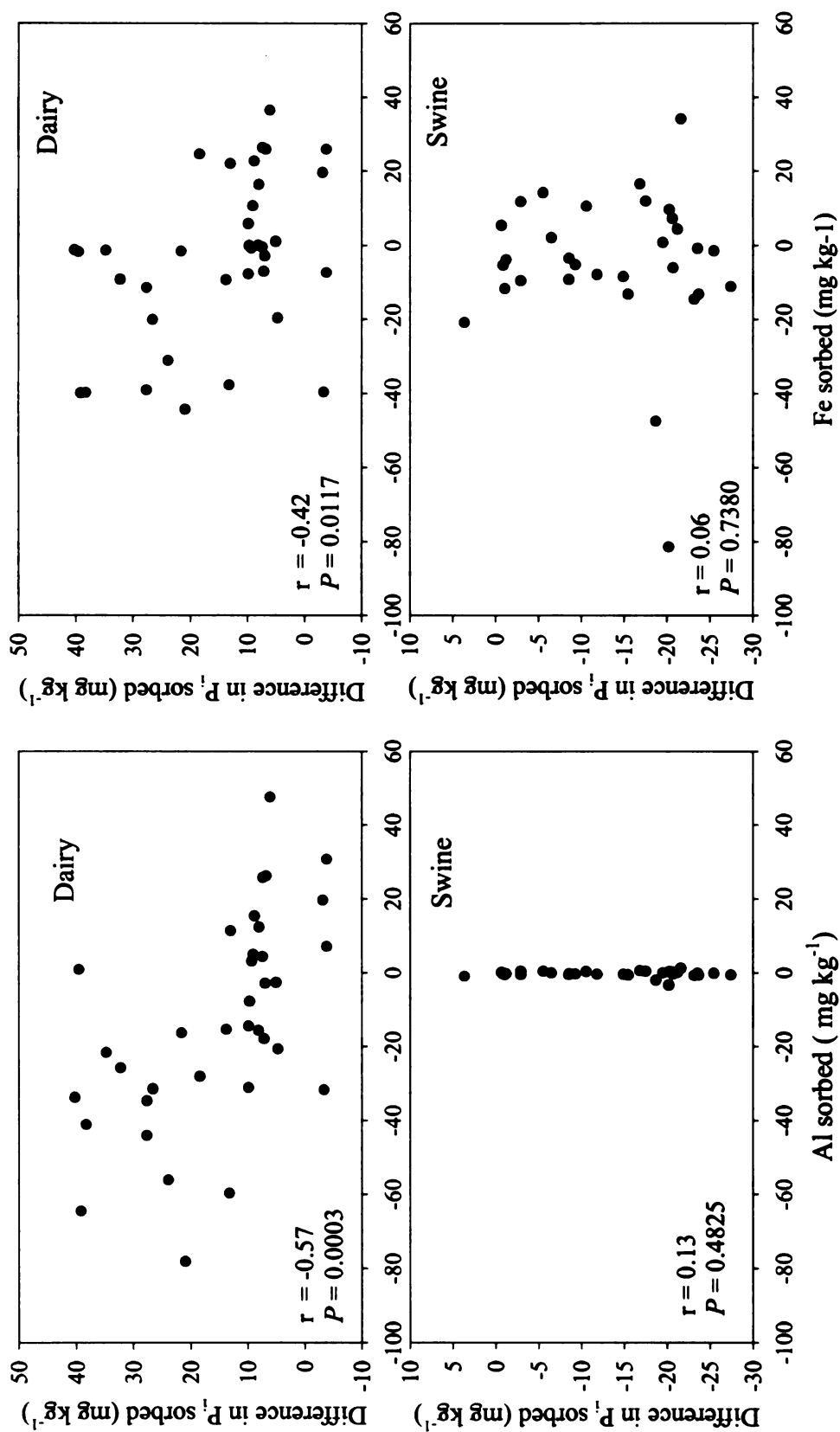


Figure F.4. Correlation of desorbed Fe or Al and the difference in P_i sorption for manure slurries and KH_2PO_4 for Oshtemo soil where r is the correlation coefficient and P is the significance of the correlation.

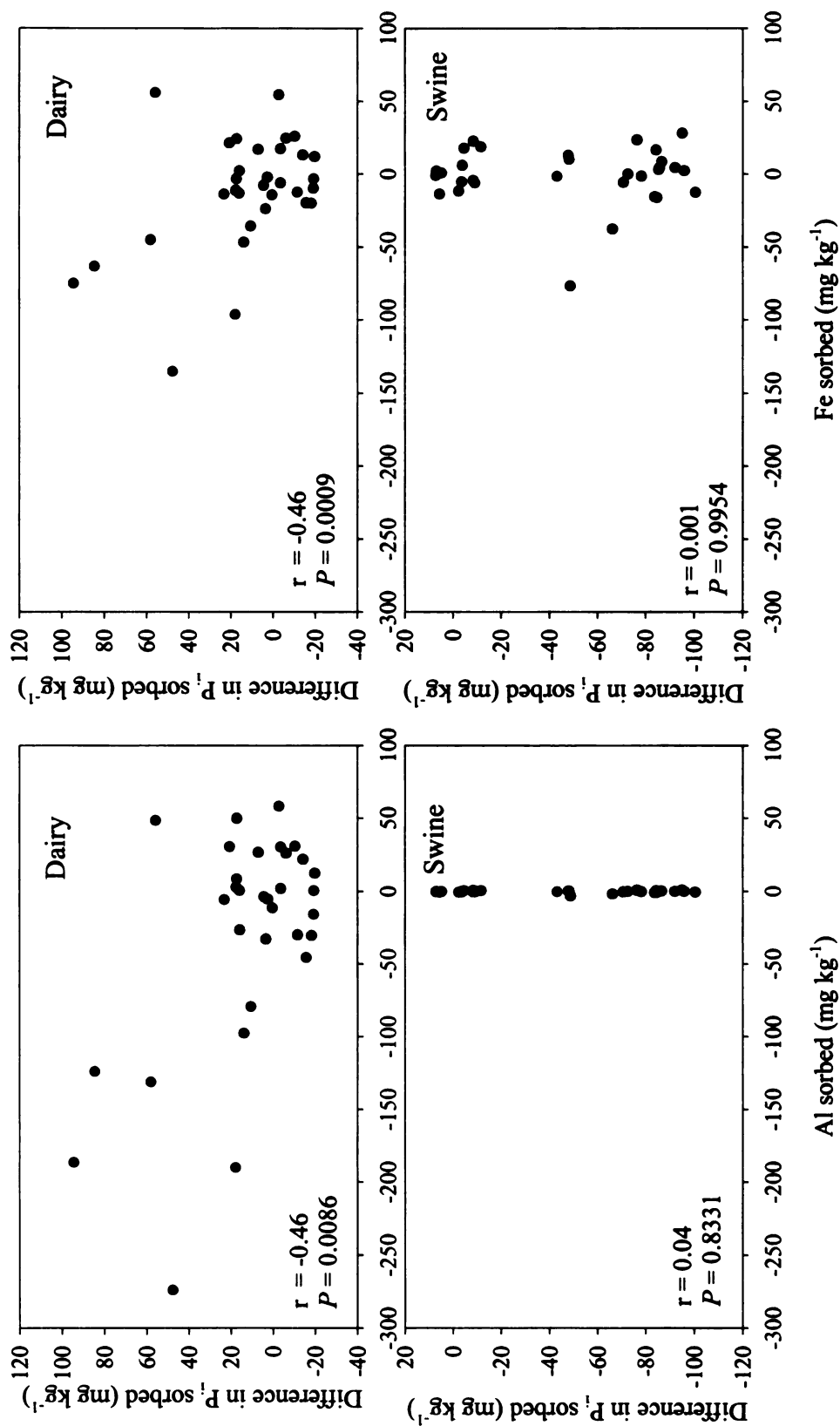


Figure F.5. Correlation of desorbed Fe or Al and the difference in P_i sorption for manure slurries and KH_2PO_4 for Parkill soil where r is the correlation coefficient and P is the significance of the correlation.

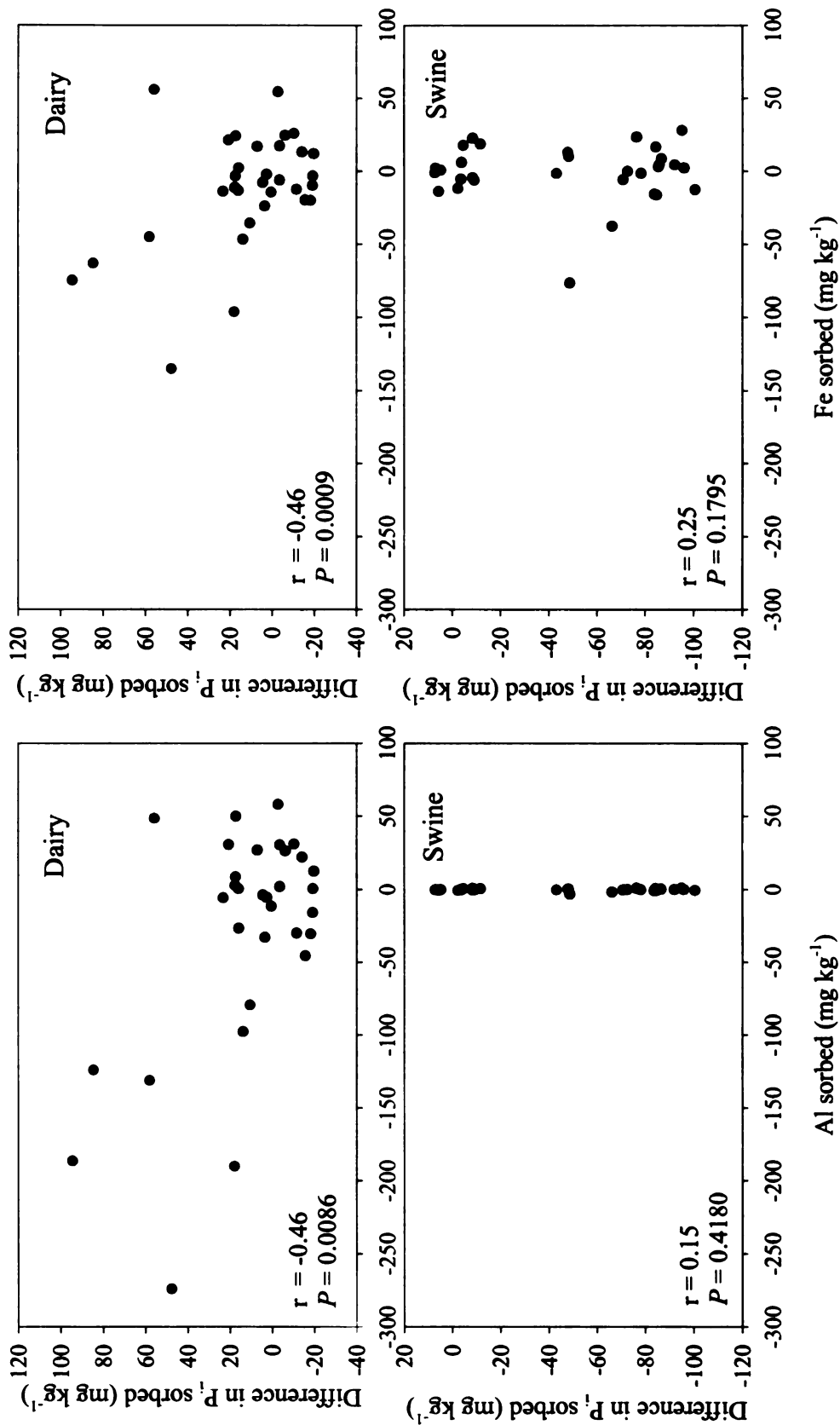


Figure F.6. Correlation of desorbed Fe or Al and the difference in P_i sorption for manure slurries and KH_2PO_4 for Spinks soil where r is the correlation coefficient and P is the significance of the correlation.

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