



Phosphorus mobility and degree of saturation in oxisol under no-tillage after long-term dairy liquid manure application

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ABSTRACT

The main way of manure use is its application to croplands near livestock farms as a nutrient source to enhance crop production. However, if incorrectly applied, the manure can become an environmental problem due to phosphorus losses to water bodies. This study aims: i) to assess the mobility of phosphorus downward in the soil profile; ii) to evaluate the long-term influence of dairy liquid manure (DLM) application under no-tillage on phosphorus adsorption; and iii) to suggest an environmental threshold for soil phosphorus. The experiments were conducted at two experimental stations of the ABC Foundation, Paraná state, Brazil. One site had a dystrophic red-yellow oxisol (sandy oxisol), sandy clay loam texture soil with 13% slope. The other site had a dystrophic oxisol (clayey oxisol), clayey texture soil with 10% slope. The experiments started in November 2005 and May 2006 in the sandy oxisol and clayey oxisol soils, respectively, in areas where the no-tillage system had been practiced for over 15 years. Treatments consisted of four rates of DLM (0, 60, 120, 180 m³ ha⁻¹ year⁻¹). Soil samples were collected in 2014 at six depths (0–10; 10–20; 20–30; 30–40; 40–50; 50–60 cm). The effect of DLM on downward phosphorus mobility in the soil profile was observed up to 50 cm in the sandy oxisol soil. In the clayey oxisol soil, the phosphorus in soil solution was affected by DLM application up to 20 cm. A reduction in the binding energy was observed in both soils with the application of DLM. The maximum phosphorus adsorption capacity decreased only in the sandy oxisol soil. It was possible to determine the change point only for the sandy oxisol soil at 62.2% of DPS_{Resin} (degree of phosphorus saturation with resin extraction) and 34.2% of DPS_{Mehlich} (degree of phosphorus saturation with Mehlich extraction). This corresponds to 188 mg kg⁻¹ of soil resin P and 103 mg kg⁻¹ of soil Mehlich–1 P, at the soil surface (0–10 cm). These values for this type of soil, are recommended as an environmental threshold for phosphorus.

1. Introduction

Brazil is the fifth largest milk producer in the world, and Paraná state, Southern Brazil, is the major milk producer in Brazil (IBGE, 2014). Paraná state is the pioneer in adoption and diffusion of the no-tillage system in Brazil, with almost 50% of agricultural fields under this system (Motter and Almeida, 2015). The manure produced in this state is commonly applied to no-tillage croplands without incorporating into the soil, which promotes accumulation of P at the soil surface (Sharpley, 2003).

The long-term manure amendment has reduced costs of mineral fertilizers and improved the physical and chemical properties of the soil (Chang et al., 1991; Mellek et al., 2010; Sommerfeldt et al., 1998). However, in areas with large concentrations of confined animals, manure also plays an important role in nitrogen and phosphorus losses

to water bodies (Carpenter et al., 1998). When applied without technical criteria, i.e., excessive applications, manure can turn into an environmental problem (Sharpley and Wang, 2014).

Nutrients from the application of manure in croplands can be transported from soil to water via the surface and subsurface, accelerating the process of eutrophication, which has become a common and growing problem in rivers, lakes, estuaries, and oceanic coasts (Smith et al., 1999). Phosphorus is considered the limiting element of the eutrophication process in freshwater bodies, it promotes the biological ability of some blue-green algae to fix atmospheric nitrogen, thus providing nitrogen to the aquatic system (Schindler et al., 2008).

The risk of phosphorus contamination in water bodies is mostly associated with its transport via surface runoff due to its great capacity for adsorption with iron and aluminium oxides, and clay minerals (Fontes and Weed, 1996; Novais and Smith, 1999). It is also known that

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Table 1
Particle size distribution and chemical properties of the soils investigated (0–20 cm).

Soils	Clay g kg ⁻¹	Silt	Sand	pH CaCl ₂	TOC g kg ⁻¹	Al cmol _c kg ⁻¹	H + Al	Ca	Mg	K	CEC	P _{Mehlich} mg kg ⁻¹
Sandy Oxisol	228	33	739	5.1	13.2	0	3.45	3.7	0.7	0.2	8.05	19
Clayey Oxisol	701	111	188	5.4	25.6	0	4.4	5	1.4	0.3	11.10	4

TOC = total organic carbon; CEC = cation exchange capacity.

the excessive input of organic and inorganic phosphorus can result in significant losses of phosphorus via both surface and subsurface flow (Pizzeghello et al., 2011; Sims et al., 1998).

The risk of phosphorus transport from soil to water bodies can be associated to its degree of saturation in the soil (Heckrath et al., 1995). The critical concentration in soil solution occurs before the complete saturation of phosphorus sorption sites in the soil (Breeuwsma and Silva, 1992), and represents the limit at which the soil is no longer a phosphorus sink and becomes a phosphorus source. This critical concentration is called by many authors a 'change point' or 'threshold', from which the risk of phosphorus loss to water bodies increases (Mcdowell and Sharpley, 2001; Nair et al., 2004). The change point is an excellent tool to estimate the vulnerability of phosphorus loss, however, to better estimate phosphorus environmental risk, several other factors should be considered (Sharpley and Wang, 2014).

The degree of phosphorus saturation (DPS) of the soil was initially used in the Netherlands as a tool to predict environmental limits of phosphorus in sandy soils. It was calculated as the ratio of [P] to [Fe + Al], extracted from the soil by oxalate, and related to water-soluble phosphorus (WSP) in soil (Breeuwsma and Silva, 1992). Studies involving the DPS have been extended to the entire world with modifications (Nair, 2014). Sims et al. (2002) calculated the DPS as [P] to [Fe + Al], extracted by Mehlich-3, and related it to dissolved reactive phosphorus obtained in a leaching column and runoff simulation. Nair et al. (2004) obtained the DPS as [P] to [Fe + Al], extracted by Mehlich-1 and related to WSP and 0.01 M CaCl₂-extractable P.

Some authors used the maximum phosphorus adsorption capacity (MPAC) of the soil estimated by the Langmuir adsorption isotherm to determine DPS (Abdala et al., 2012; Kleinman and Sharpley, 2002; Mcdowell and Sharpley, 2002; Pautler and Sims, 2000; Sharpley, 1995). According to Mcdowell and Sharpley (2002), the phosphorus in soil extracts used in the DPS calculation is usually specific for certain types of soils. Phosphorus adsorption isotherms also reflect the physico-chemical properties of soils through their parameters (MPAC and binding energy), which are fundamental in determining the phosphorus mobility potential of the soil (Holford et al., 1997; Mcdowell and Sharpley, 2002). Thus, it is recommended to use MPAC to obtain the DPS.

Phosphorus adsorption in soils is strongly affected by the texture (Fontes and Weed, 1996). Generally, sandy soils have a lower MPAC when compared to clay soils (Oliveira et al., 2014; Valladares et al., 2003). The continuous application of manure can alter the phosphorus-binding energy and MPAC (isotherm Langmuir parameters) due to occupation of the adsorption sites by organic matter where phosphorus could be sorbed, leading to greater phosphorus mobility and availability in the soil (Eghball et al., 1996; Guppy et al., 2005).

With dairy farming increasing worldwide, information on the impact of using dairy manure as an amendment on croplands that leads to pollution potential of water bodies is needed. This study aims (1) to evaluate the application of dairy liquid manure (DLM) over the long term (nine years) on phosphorus adsorption and mobility in oxisol soil of different textures (sandy and clayey) under no-tillage and (2) to suggest an environmental threshold for soil phosphorus.

2. Materials and methods

2.1. Experimental site

The experiments were conducted at two experimental stations of the ABC Foundation for Agricultural Assistance and Technical Divulcation, Paraná state, Brazil: one at Ponta Grossa (25°00'35"S, 50°09'16"W, 890 m altitude) on a dystrophic red-yellow oxisol (sandy oxisol), sandy clay loam texture soil with 13% slope, and the other at Castro (24°51'50"S, 49°56'25"W, 1027 m altitude) on a dystrophic oxisol (clayey oxisol), clayey texture soil with 10% slope. The regional climate is classified as Cfb – humid subtropical climate mesothermal (Köppen), with mild summers and an average annual rainfall of 1554 mm, without a dry season (Caviglione et al., 2000).

Experimental plots were installed in November 2005 and May 2006 at Ponta Grossa and Castro, respectively, where no-tillage system had been practiced for more than 15 years. Crop rotation involved black oat (*Avena strigosa* Schreb.) and wheat (*Triticum aestivum* L.) in the winter and soybean (*Glycine max* (L.) Merr.) and maize (*Zea mays* L.) in the summer. The no-tillage had been practiced at the two research sites prior to the first application of liquid dairy manure for more than 15 years, then, no-tillage practices continued to be applied along with annual applications of liquid dairy manure for the next 10 years. The soil properties before the beginning of the experiments are presented in Table 1.

Treatments consisted of four annual rates of DLM (0, 60, 120, 180 m³ ha⁻¹ year⁻¹). The experiment was established as a randomized complete block design with four replications, and plots were 29.8 m² (3.5 m by 9 m). Each annual DLM rate was split into two applications: (i) half in the winter crop and (ii) half in the summer crop. The DLM was brought from a dairy farm near the experimental site and manually applied on the soil surface with a watering can. The chemical properties of the DLM applied since the beginning of the experiments (2005–2014) are provided in Tables 2 and 3. The amount of N, P, and K (annual average for winter plus summer crops) applied by DLM and by mineral fertilizers are in Table 4. Besides DLM, mineral fertilizers (NPK) were applied in the same amount for all treatments following the soil test and crop needs (Rajj et al., 1997). Mineral fertilization without considering the quantity of nutrients applied by manure is a common practice among farmers, so the experiment was designed to simulate this condition and to investigate the environmental risk of this overfertilization.

2.2. Soil sampling and analyses

Soil samples were collected in July 2014 at Castro and in October 2014 at Ponta Grossa at six depths (0–10; 10–20; 20–30; 30–40; 40–50; 50–60 cm). All soil samples were air-dried and sieved through a 2-mm sieve. Soil phosphorus was extracted using an anion exchange resin (resin P) (Rajj et al., 1997) and Mehlich-1 (Marques and Motta, 2003). Total soil phosphorus was extracted from soil samples using the USEPA 3051 method (USEPA, 2007) and determined by ICP-OES.

WSP extraction was performed in topsoil samples (0–10 cm), with deionised water at a 1:10 soil-to-water ratio, which were then shaken for one hour. After this, the samples were centrifuged and filtered through a cellulose membrane of 0.45 µm. The same procedure was used for extraction of phosphorus using a 0.01 mol L⁻¹ CaCl₂ solution

Table 2
Chemical properties of the dairy liquid manure (DLM) applied from year 2005–2014 for the experimental area at Ponta Grossa – PR (sandy oxisol).

Date	Dry Matter			Total N			Total P			Total K			Total Cu			Total Zn		
	(g L ⁻¹)						(mg L ⁻¹)											
Dec-05	16	0.38	0.22	0.84	nd	nd												
Apr-06	86.4	2.2	0.84	1.66	nd	nd												
Sep-06	68.4	0.68	0.69	1.85	nd	nd												
Jun-07	110.2	2.3	0.63	1.87	nd	nd												
Nov-07	72	1.57	0.6	2.37	20.4	20.5												
Jun-08	108.2	2.14	0.69	2.13	42.7	nd												
Aug-08	97.3	2.08	0.6	1.79	23	nd												
Jul-09	73.4	1.71	0.76	1.91	24.6	29.6												
Dec-09	158.2	2.42	0.65	3.78	12.2	34.9												
May-10	71.4	1.68	0.79	2.28	9.65	38.6												
Nov-10	129.4	2.76	1.22	3.15	nd	39												
Aug-11	15.9	1.4	0.13	1.08	31.3	48.1												
Jan-12	43.4	1.18	0.54	0.75	33.3	23												
Jul-12	48.6	1.9	0.52	0.75	3.08	26.8												
Jan-13	54.9	1.15	0.37	0.04	2.65	44.3												
Jul-13	31.8	2.8	0.3	0.38	2.63	30.2												
Jan-14	58.6	1.1	0.39	4.15	2.86	40.7												
Jul-14	nd	nd	nd	nd	nd	nd												
11/2014	69.8	2.9	1.27	1.99	9.78	37.3												
Average	73	1.8	0.62	1.82	16.8	34.4												
Standard Deviation	36.6	0.7	0.29	1.07	13.5	8.5												

nd = not determined.

Table 3
Chemical properties of the dairy liquid manure (DLM) applied from year 2006–2014 for the experimental area at Castro – PR (clayey oxisol).

Date	Dry Matter			Total N			Total P			Total K			Total Cu			Total Zn		
	(g L ⁻¹)						(mg L ⁻¹)											
May-06	90.5	1.82	0.77	3.46	nd	nd												
Oct-06	75.5	1.74	0.61	2.35	nd	nd												
May-07	43.3	0.95	0.41	1.48	nd	nd												
Nov-07	89.6	2.02	0.72	3.04	7.33	49.6												
Aug-08	87.1	1.75	0.61	2.85	5.66	31.6												
Jan-09	46.7	1.1	0.32	1.57	3.54	17.9												
Aug-09	51	0.94	0.56	1.2	3.53	18.7												
Nov-09	44.9	2.6	0.92	1.91	6.56	28.7												
Jul-10	85.5	1.56	0.7	3.22	10.1	39.3												
Jan-11	93.1	1.74	0.84	4.14	7.04	36.5												
Aug-11	113	2.29	0.83	4.19	nd	35.7												
Nov-11	94	1.85	0.69	3.71	7.82	47.6												
Aug-12	87.3	2.23	0.65	4.09	10.1	49.3												
Jan-13	73.7	1.56	0.54	0.13	5.6	35.8												
Jun-13	79.1	1.66	0.61	3.91	6.22	32.5												
Nov-13	71.1	1.44	0.43	3.27	4.54	3												
Jul-14	94.5	5.2	0.87	2.74	7.01	73.1												
Jan-15	91.4	4.2	0.7	3.49	5.69	61.6												
Average	78.4	2.04	0.65	2.82	6.48	37.5												
Standard Deviation	19.9	1.08	0.16	1.16	1.94	17												

nd = not determined.

Table 4
Amount (annual average for winter plus summer crops) of nitrogen (N), phosphorus (P) and potassium (K) applied via dairy liquid manure and via mineral fertilizers for the experimental area at Ponta Grossa-PR (sandy oxisol) and Castro-PR (clayey oxisol).

Soils	60 m ³ ha ⁻¹ year ⁻¹			120 m ³ ha ⁻¹ year ⁻¹			180 m ³ ha ⁻¹ year ⁻¹			Mineral		
	N	P	K	N	P	K	N	P	K	N	P	K
	kg ha ⁻¹ year ⁻¹											
Sandy Oxisol	111	36	106	223	71	211	334	107	317	140	48	90
Clayey Oxisol	122	39	169	244	79	338	367	118	508	132	46	82

(CaCl₂-P). The concentrations of WSP and CaCl₂-P were determined using the colorimetric method (APHA, 2005). Soil solution samples were extracted in accordance with the saturation paste methodology described by Rhoades (1996) and passed through a 0.45-µm cellulose membrane filter. Phosphorus in the soil solution (PSS) was measured directly by ICP-OES.

2.3. Phosphorus sorption isotherms

Phosphorus sorption isotherms were obtained at the soil surface (0–10 cm) for each treatment according to Alvarez and Fonseca (1990). An interval of 11 phosphorus concentrations was predefined (sandy oxisol soil: 0, 3, 6, 9, 15, 21, 27, 33, 42, 51, 60 mg L⁻¹ P; clayey oxisol soil: 0, 10.5, 21, 31.5, 52.5, 73.5, 94.5, 115.5, 147, 178, 210 mg L⁻¹ P), based on the PSI (phosphorus sorption index). The PSI was obtained by shaken 2.5 g of soil (air-dried < 2 mm) with 25 mL of 0.01 M CaCl₂ solution containing 60 mg L⁻¹ P (as KH₂PO₄) for one hour. The phosphorus isotherms were obtained by adding 25 mL of 0.01 M CaCl₂ solution containing phosphorus (as KH₂PO₄) at predefined concentrations with 2.5 g of soil (air-dried and < 2 mm) followed by shaking it at 120 rpm for 24 h. After that, the samples were centrifuged and filtered, and the equilibrium phosphorus concentration was determined using the colorimetric method (APHA, 2005).

The equilibrium phosphorus concentrations and the phosphorus sorbed by the soil were fitted according to the nonlinear Langmuir model by the least squares method using the Solver (Excel 2010[®]) to obtain *k* and *b* values according to the equation: $q = (kbC)/(1 + kC)$, where *q* = P sorbed (mg kg⁻¹), *k* = P binding energy (L mg⁻¹), *b* = soil MPAC (mg kg⁻¹), and *C* = equilibrium concentration of P.

2.4. Degree of phosphorus saturation (DPS) and change point (CP)

The DPS in the soil was calculated according to the following expressions:

$$DPS_{Re\ sin} = \frac{Pre\ sin}{MPAC} \times 100 \quad DPS_{Mehlic-1} = \frac{P_{mehlic-1}}{MPAC} \times 100$$

The change point in DPS was obtained by plotting the following relationship: a) DPS vs. PSS, b) DPS vs. WSP, c) DPS vs. CaCl₂-P. These relationships were modelled as segmented linear regressions of two segments with different angular coefficients, with the change point as their intercept. As dictated by the equations, the first (1) was the line segment below the change point, and the second (2) was the segment above the change point:

$$PSS; WSP; CaCl_2 - P(DPS) = \frac{y_1 \times (CP - DPS) + y_2 \times (DPS - t_1)}{CP - t_1}, \quad t_1 \leq DPS \leq CP \tag{1}$$

$$PSS; WSP; CaCl_2 - P(DPS) = \frac{y_2 \times (t_2 - DPS) + y_3 \times (DPS - CP)}{t_2 - CP}, \quad CP \leq DPS \leq t_2 \tag{2}$$

Where CP is the change point in DPS, *t*₁ is the highest value for DPS, *t*₂ is the lowest value, and *y*₁, *y*₂, and *y*₃ are model adjustment variables. The four variables (*y*₁, *y*₂, *y*₃, and CP) were estimated by the segmented

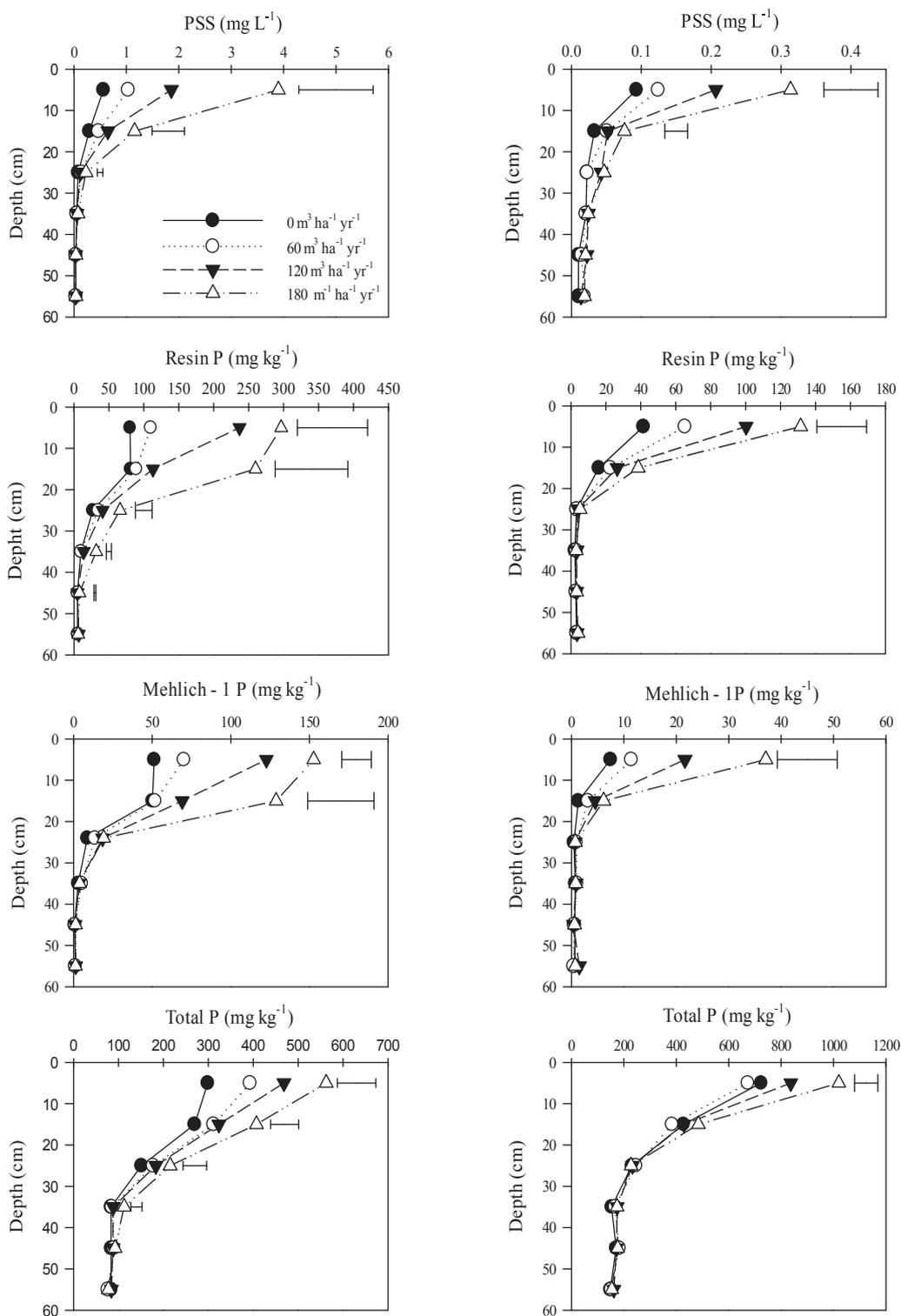


Fig. 1. Concentration of phosphorus in soil solution (PSS), resin P, Mehlich-1 P and total P at 0–10, 10–20, 20–30, 30–40, 40–50, 50–60 cm soil layers (left = sandy oxisol soil; right = clayey oxisol soil) as affected by application of dairy liquid manure at rates of 0, 60, 120, 180 m³ ha⁻¹ year. The horizontal bar represents the least significant difference, according to Tukey's test ($p < 0.05$).

linear regression model with the SIGMAPLOT 12.0 (Systat Software Inc.) statistical programme. The change point in soil test P value was obtained by the linear regression of DPS (DPS_{Mehlich-1} and DPS_{Resina}) vs. soil test P (P_{Mehlich-1} and P_{Resina}). The environmental threshold was defined as the change point calculated by the relationship between DPS and PSS.

2.5. Statistical analyses

Data normality was assessed by the Shapiro–Wilk test. For the

phosphorus data, mobility in the soil was used for the Tukey test ($p < 0.05$), and linear regression analysis was performed for the relations between P extracted by different methods. The statistical programmes used were ASSISTAT 7.7 Beta and SIGMAPLOT 12.0 (Systat Software Inc.).

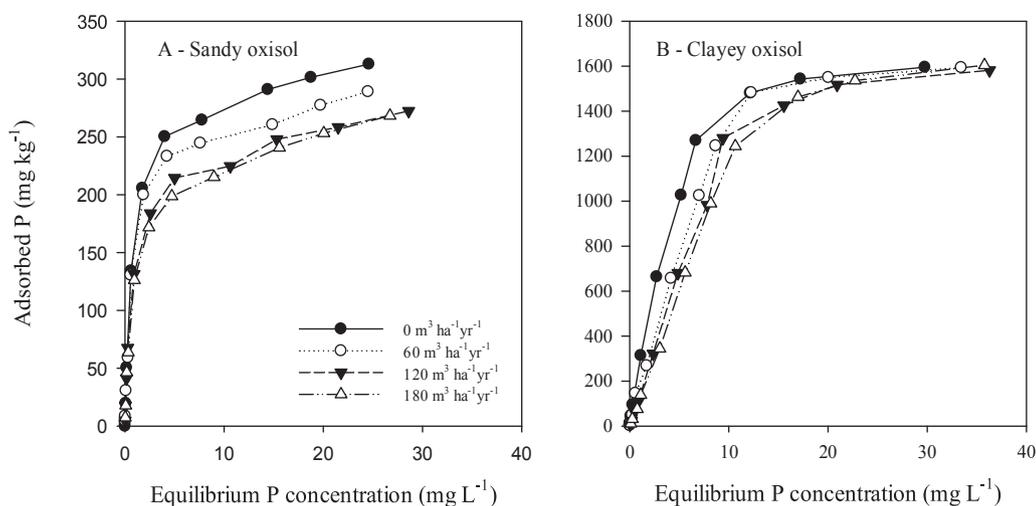


Fig. 2. Adsorbed P (mg kg^{-1}) as a function of P in the equilibrium solution in the sandy oxisol soil (A) and clayey oxisol soil (B) at soil surface (0–10 cm) layer after application of dairy liquid manure at rates of 0, 60, 120, 180 $\text{m}^3 \text{ha}^{-1} \text{year}^{-1}$.

Table 5
Parameters *b* (maximum phosphorus adsorption capacity) and *k* (binding energy) estimated by the Langmuir equation in the soil surface (0–10 cm) layer of the clayey and sandy oxisol soils after long term applications of dairy liquid manure (DLM) at rates of 0, 60, 120, 180 $\text{m}^3 \text{ha}^{-1} \text{year}^{-1}$.

Soils	DLM	Parameters ^a	
		<i>b</i>	<i>k</i>
Clayey Oxisol	$\text{m}^3 \text{ha}^{-1} \text{year}^{-1}$	mg kg^{-1}	L mg^{-1}
	0	1730 a	0.375a
	60	180 a	0.344ab
	120	1820 a	0.234b
Sandy Oxisol	180	1850 a	0.248b
	0	330 a	0.614a
	60	308 b	0.458b
	120	294 c	0.347bc
	180	299 c	0.242c

^a $p < 0.05$.

3. Results and discussion

3.1. Phosphorus in soil and soil solution

Enhancement of phosphorus concentrations at depth as a result of DLM application was observed, indicating phosphorus mobility downward in the soil profile (Fig. 1). This was expected because of the long-term (continuous) manure application (Abdala et al., 2012; Leinweber et al., 2002). There was a clear influence of soil texture on phosphorus in the soil solution in response to DLM application. The concentrations of phosphorus in the soil solution in the sandy and clayey oxisol soils ranged from 0.03 to 3.90 mg L^{-1} and 0.009 to 0.313 mg L^{-1} , respectively, with effect of DLM up to 30 cm in depth in the sandy oxisol soil and 20 cm in depth in the clayey oxisol soil. These results confirm the clay content as a major player in the phosphorus buffering capacity. Over the experiment (nine years), the amount of phosphorus added to each soil was almost the same, with 1475 and 1463 kg ha^{-1} of P for the sandy and clayey oxisol soils, respectively, by the highest rate of DLM (180 $\text{m}^3 \text{ha}^{-1} \text{year}^{-1}$) plus mineral fertilization.

In Brazil, soil P-tests for phosphorus fertilization in agricultural production are done by phosphorus extracted with Mehlich-1 or resin (Rajj et al., 1997; SBCS, 2004). In our study, both soil P-tests showed the influence of DLM (Fig. 1). The results also confirmed the higher capacity of resin to extract and recover the applied phosphorus than Mehlich-1 (Rajj et al., 1997). The distribution of P extracted in the profile was similar for both extractors; however, the resin extractor better demonstrated the effect of manure in the soil profile, especially in the sandy soil. The sandy soil showed changes in phosphorus

availability well below the first layer, suggesting high mobility downward in the soil profile.

The effect of DLM application was also observed for total phosphorus content (Fig. 1). The results from total phosphorus confirmed the accumulation within the 0–10 cm layer for clayey soil, while in the sandy soil the influence of DLM extended to 30–40 cm in depth. In this way, resin extractable P seems to be closely related to total phosphorus. The average concentration of total phosphorus in sandy and clayey oxisol soils ranged from 76 to 562 mg kg^{-1} and 148 to 1020 mg kg^{-1} , respectively.

In general, the phosphorus mobility in the clayey oxisol soil was restricted to 0–10 cm in depth, whereas for the sandy oxisol soil the influence reached 40–50 cm in depth. Studies with long-term application of manure in various soil types also showed higher mobility of phosphorus in sandy soils (Abdala et al., 2012; Eghball et al., 1996; Mozaffari and Sims, 1994; Novak et al., 2000). In our study, both soils, under the no-tillage system, received surface application of DLM, which is expected to result in higher soil P content at the surface layer. The higher phosphorus adsorption capacity of the clayey oxisol soil, however reduced the phosphorus mobility in the soil profile. The leaching of fine particles of inorganic phosphorus suspended in the liquid manure could be one reason for the increase of phosphorus at soil depth (Fordham and Schwertmann, 1977; Sims et al., 1998), mainly in sandy soils. Considering the soil condition under long-term no-tillage (25 years), the transport of phosphorus from the surface to subsurface by preferential flow could also affect the phosphorus mobility (Leinweber et al., 2002).

3.2. Phosphorus adsorption isotherms

The adsorption of phosphorus in relation to its equilibrium concentration in the solution for both soils (Fig. 2) was well described by the nonlinear Langmuir model. Phosphorous adsorption was higher in the clayey oxisol soil, but there were no significant differences between the rates of DLM in determining MPAC (Table 5). However, the binding energy (*k* parameter) decreased with increasing rates of DLM with the rates of 120 and 180 $\text{m}^3 \text{ha}^{-1}$ (0.234 and 0.248 L mg^{-1} , respectively) resulting in statistically lower values than for the control (0.375 mg L^{-1}).

In the sandy oxisol soil, a reduction in MPAC was observed with increasing rates of DLM (Table 5). The MPAC value for the control treatment (330 mg kg^{-1}) was higher than that observed for treatments of 60, 120, and 180 $\text{m}^3 \text{ha}^{-1}$ (308, 294, and 299 mg kg^{-1}). The binding energy (*k* parameter) also decreased with increasing rates of DLM. The highest value was found for the control treatment (0.614 mg L^{-1}), and the lowest value was observed for the highest DLM rate (0.242 mg L^{-1}).

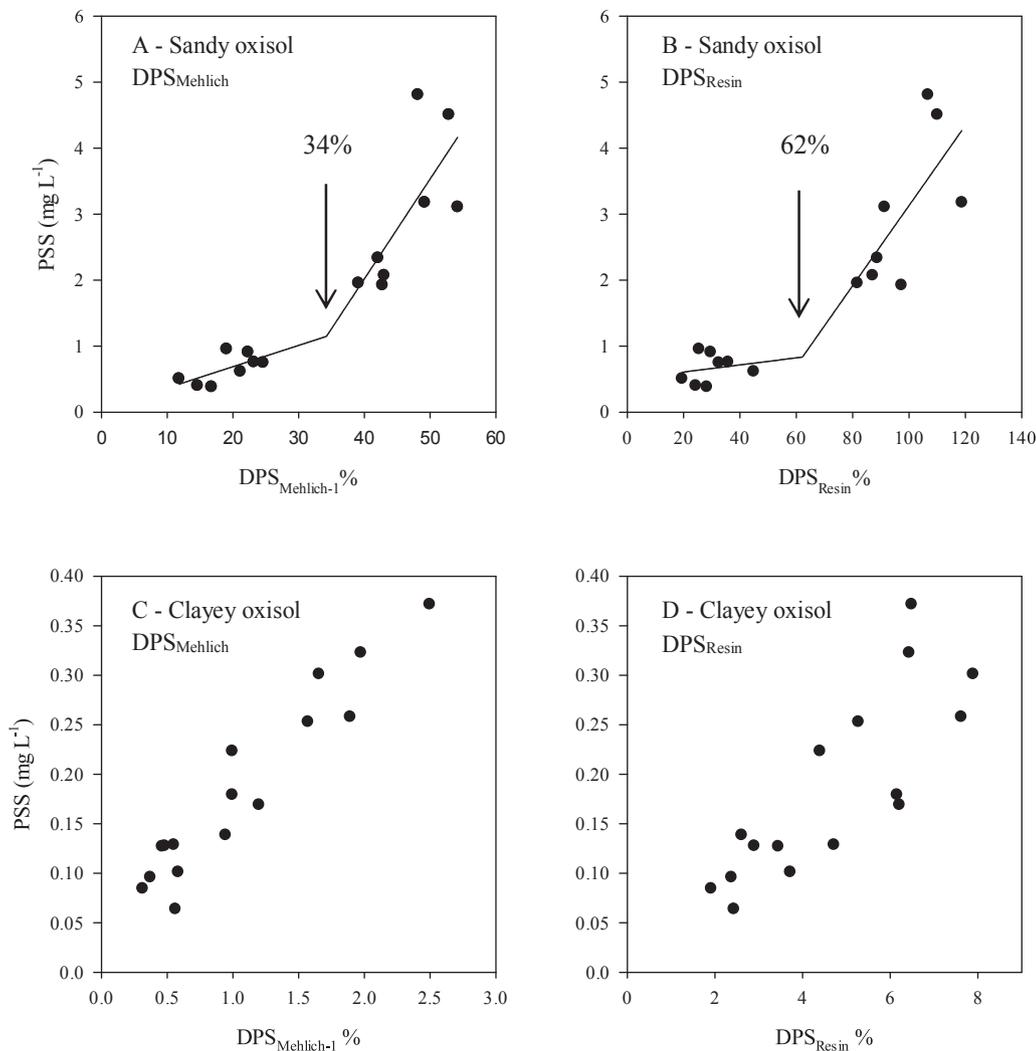


Fig. 3. Relationship between concentration of phosphorus in the soil solution (PSS) and degree of phosphorus saturation (DPS) in the sandy and clayey oxisol soils (A = sandy oxisol and $DPS_{Mehlich}$; B = sandy oxisol and DPS_{Resin} ; C = clayey oxisol and $DPS_{Mehlich}$; D = clayey oxisol and DPS_{Resin}). Change point indicated by arrow.

Table 6
Fitted segmented linear regression model to phosphorus in soil solution (PSS) and degree of phosphorus saturation ($DPS_{Mehlich}$ and DPS_{Resin}) in the sandy oxisol soil.

Equation	R^2
$PSS = ((0.42 \times (34.22 - DPS_{Mehlich}) + 1.14 \times (DPS_{Mehlich} - 11.78)) / (34.22 - 11.78)); DPS \leq 34.22$	0.86*
$PSS = ((1.14 \times (54.18 - DPS_{Mehlich}) + 4.16 \times (DPS_{Mehlich} - 34.22)) / (54.18 - 34.22)); DPS > 34.22$	
$PSS = ((0.60 \times (62.20 - DPS_{Resin}) + 0.83 \times (DPS_{Resin} - 19.39)) / (62.20 - 19.39)); DPS \leq 62.20$	0.83*
$PSS = ((0.83 \times (118.72 - DPS_{Resin}) + 4.26 \times (DPS_{Resin} - 62.20)) / (118.72 - 62.20)); DPS > 62.20$	

Table 7
Linear regression model to obtain change point (CP) in soil test P value ($P_{Mehlich}$ and P_{Resin}) from change point in DPS ($DPS_{Mehlich}$ and DPS_{Resin}) in the sandy oxisol soil.

Equation	R^2
$CP_{P_{Mehlich}} = (2.8454 \times CP_{DPS_{Mehlich}}) + 5.9343$	0.99*
$CP_{P_{Resin}} = (2.8909 \times CP_{DPS_{Resin}}) + 7.9042$	0.99*

CP = change point; DPS = degree of phosphorus saturation.

* $p < 0.0001$.

The MPAC reduction with DLM application in the sandy oxisol soil is explained by filling of the phosphorus adsorption sites by the organic matter from the manure, which involves the same adsorption reaction

with soil particles (ligand exchange) (Guppy et al., 2005). Binding energy decreased in both soils with the application of DLM; however, the effect was greater in sandy oxisol soil. This reduction indicates that phosphorus mobility will increase with manure application. Field et al. (1985) also observed a reduction in binding energy with manure application in a clay soil, but no effect was verified on MPAC. In a long-term experiment (40 years) with the application of cattle manure, Eghball et al. (1996) observed reduced binding energy and MPAC in a sandy soil, up to 90 cm in depth.

The greater capacity for phosphorus adsorption in a clayey oxisol soil probably resulted in no effect on the Langmuir parameters with application of DLM over the long term. For this soil, the risk of phosphorus saturation and phosphorus mobility via subsurface would be minimal. However, in the sandy oxisol soil, the observed effect on the Langmuir parameters with application of DLM over the long term was evident, with a reduction of phosphorus sorption sites as well as a lower binding energy. This results in greater susceptibility of this soil to phosphorus mobility.

3.3. Change point

The results show a relationship between PSS and $DPS_{Mehlich}$ and between PSS and DPS_{Resin} for sandy oxisol soil (Fig. 3). The change point was obtained at 34.2% $DPS_{Mehlich}$, which corresponds to 103 mg kg⁻¹ of $P_{Mehlich}$ and 1.14 mg L⁻¹ of PSS. The change point with DPS_{Resin} was at 62.2%, corresponding to 188 mg kg⁻¹ of P_{Resin} and 0.83 mg L⁻¹ of PSS. The estimated parameters and R^2 values for the

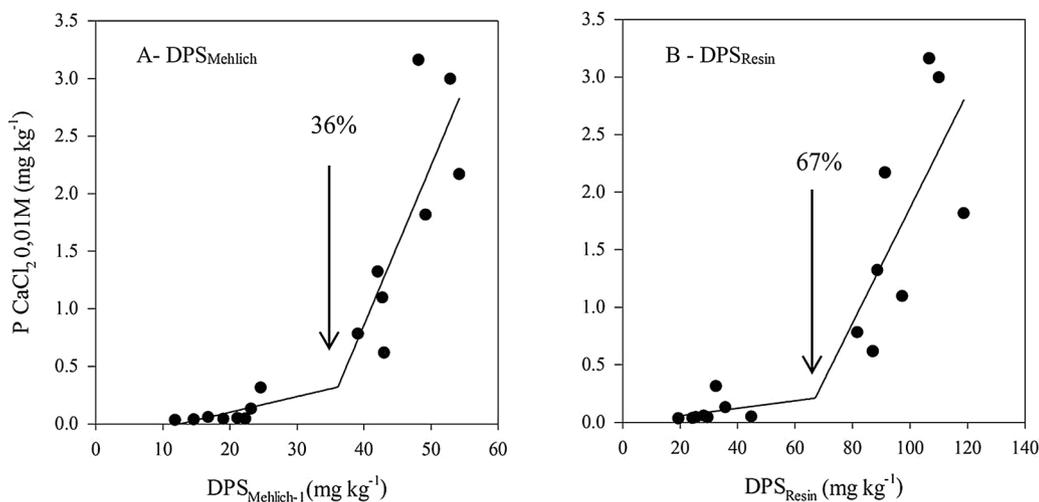


Fig. 4. Relationship between concentration of soil phosphorus extracted by CaCl₂ and degree of phosphorus saturation (A = DPS_{Mehlich}; B = DPS_{Resin}) in the sandy oxisol soil. Change point indicated by arrow.

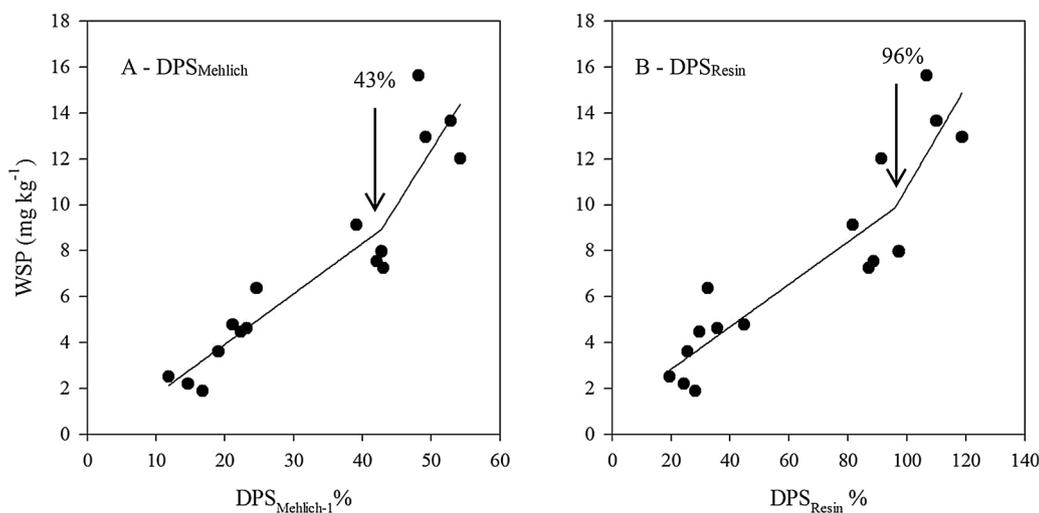


Fig. 5. Relationship between concentration of water soluble phosphorus (WSP) and the degree of phosphorus saturation (A = DPS_{Mehlich}; B = DPS_{Resin}) in the sandy oxisol soil. Change point indicated by an arrow.

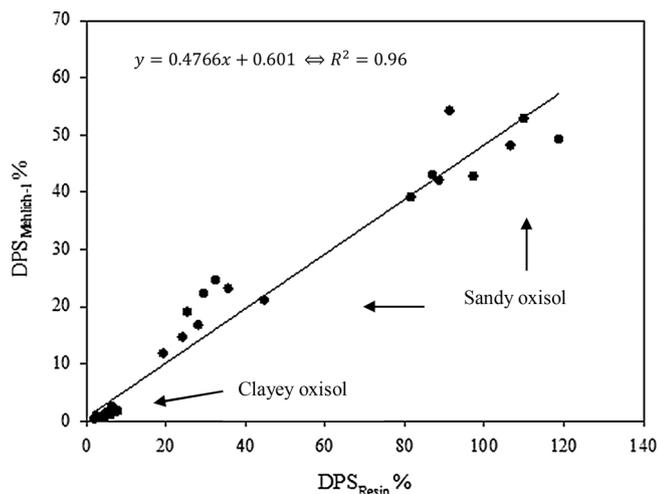


Fig. 6. Relationship between degree of phosphorus saturation (DPS) calculated with Mehlich-1 P (DPS_{Mehlich}) and resin P (DPS_{Resin}) in sandy and clayey oxisol soils. ($p < 0.0001$).

fitted segmented linear regression model to obtain the change point in DPS are displayed in Table 6. The equations to obtain change point in soil test P value from change point in DPS value are displayed in Table 7.

In the clayey oxisol soil, it was not possible to determine the change

point (Fig. 3), even with high phosphorus values extracted by Mehlich-1 P and resin P; DPS_{Mehlich} did not exceed 2.4%, and DPS_{Resin} did not exceed 7.9%. This is due to the high phosphorus adsorption capacity of this soil, which is not sufficiently saturated to show a change point. In a study with a wide range of soils from the UK, New Zealand, and the US, McDowell and Sharpley (2001) also did not observe a change point, because they were not sufficiently saturated.

For the sandy oxisol soil, we observed a relationship between CaCl₂-P and DPS_{Mehlich} and between CaCl₂-P and DPS_{Resin} (Fig. 4). For DPS_{Mehlich}, the change point was 36.1%, equivalent to 109 mg kg⁻¹ of P_{Mehlich}. For DPS_{Resin}, the change point was 67%, corresponding to 202 mg kg⁻¹ of P_{Resin}. Regarding the WSP, we found a change point for DPS_{Mehlich} at 42.7%, corresponding to 127 mg kg⁻¹ of P_{Mehlich}. For DPS_{Resin}, the change point was observed at 96%, equivalent to 285 mg kg⁻¹ of P_{Resin} (Fig. 5).

The values of the change points with CaCl₂-P were very similar to PSS but higher than WSP. Sharpley and McDowell (2001) showed that CaCl₂-P is a good indicator for phosphorus losses via the subsurface and also found a lower change point in comparison to WSP. Phosphorus extraction with 0.01 M CaCl₂ aims to simulate the soil solution based on the fact that cation exchange is minimised by the use of calcium and chlorine at this concentration.

The relationship between DPS_{Mehlich} and DPS_{Resin} was linear with R² = 0.96 (Fig. 6), demonstrating that both extractors used for soil test routine analysis are appropriate in calculating the DPS. Nair et al. (2004) also found a linear relationship among the methods for calculating the DPS (Mehlich-1 P, Mehlich-3 P, and oxalate), suggesting that

any of them can be used for DPS calculations.

Various studies on change point calculated as a function of DPS can be found in the literature. In the Netherlands, a limit of 0.15 mg L^{-1} of total phosphorus in groundwater was established, corresponding to $\text{DPS}_{\text{Oxalate}}$ of 25% (Breeuwisma et al., 1995). In a study with soils from the UK, New Zealand, and the US, McDowell and Sharpley (2001) observed change points ranging from 26 to 34% of $\text{DPS}_{\text{Oxalate}}$ with $\text{CaCl}_2\text{-P}$. In a study conducted in the US in sandy soils with the application of DLM, Nair et al. (2004) indicated a change point of 38% $\text{DPS}_{\text{Mehlich}}$ with $\text{CaCl}_2\text{-P}$. In Canada, Casson et al. (2006) studied five soils with the application of cattle manure and observed a change point ranging from 11 to 51% of DPS with $\text{CaCl}_2\text{-P}$.

In Brazil, Abdala et al. (2012) studied the application of poultry litter on an ultisol and observed a change point of 22.7% $\text{DPS}_{\text{Mehlich-3}}$ with WSP. The change point values found for $\text{DPS}_{\text{Mehlich}}$ in our study are in agreement with those reported by other studies. However, no previous study reported a change point calculated by $\text{DPS}_{\text{Resin}}$ that was higher than values found in the literature with other extracts.

3.4. Environmental threshold for soil phosphorus

Soil tests of phosphorus (STP) in Brazil are generally carried out with Mehlich-1 or resin for phosphorus fertilization recommendation. In southern Brazil, there is a specific agronomic interpretation for Mehlich-1 P (SBCS, 2004) where concentrations of Mehlich-1 P higher than 24 mg kg^{-1} are classified as too high for annual crops in soils with 21–40% clay. Thus, the change point of 34.2% $\text{DPS}_{\text{Mehlich}}$ found with phosphorus in soil solution (PSS), equivalent to 103 mg kg^{-1} of Mehlich-1 P, is above the optimal agronomic soil P level for annual crops. Thus, agricultural soils with Mehlich-1 P values below the change point (103 mg kg^{-1} of Mehlich-1 P) will be in ideal conditions of soil fertility and have a low risk of environmental pollution.

Regarding the resin P, reference values for agronomic interpretation are presented by Rajj et al. (1997) for São Paulo state. Values greater than 80 mg kg^{-1} are classified as too high for annual crops. This value is below the change point of 62.2% $\text{DPS}_{\text{Resin}}$ with PSS, equivalent to 188 mg kg^{-1} of resin P. As discussed above, agricultural soils with phosphorus concentrations below the change point are optimum for plant growth with a minimal risk of environmental pollution.

Based on the results related to change point obtained by PSS, and in order to reduce the pollution potential of water bodies with phosphorus, an environmental threshold of 34.2% $\text{DPS}_{\text{Mehlich}}$ (corresponding to 103 mg kg^{-1} of Mehlich-1 P) and of 62.2% $\text{DPS}_{\text{Resin}}$ (equivalent to 188 mg kg^{-1} of resin P) is recommended for sandy oxisol soils. These are above the optimal agronomic values for annual crops. Using the environmental threshold as a management tool to control water pollution should be considered in association with other tools, such as the P index, which was developed to assess the vulnerability of areas of phosphorus loss due to source and transport factors (Sharpley and Wang, 2014).

Studies with phosphorus environmental limits in Brazil are incipient; therefore, the continuity of this research is crucial to obtain new results and to develop public policies aimed at better management practices for soil and water conservation.

4. Conclusions

Long-term dairy liquid manure (DLM) application to no-tillage fields influenced the phosphorus mobility downward in the soil profile. These changes were more evident in the sandy oxisol soil than in the clayey oxisol soil. The effect in the sandy soil with application of DLM was observed up to 50 cm in depth.

The application of DLM over the long term reduced the phosphorus binding energy in both soils, but reduction in phosphorus maximum adsorption capacity was observed only in the sandy oxisol soil.

A change point was obtained only in the sandy oxisol soil, being

34.2% $\text{DPS}_{\text{Mehlich}}$ and 62.2% $\text{DPS}_{\text{Resin}}$, both with phosphorus in soil solution (PSS), corresponding to $103 \text{ mg kg}^{-1} \text{ P}_{\text{Mehlich}}$ and $188 \text{ mg kg}^{-1} \text{ P}_{\text{Resin}}$, respectively, at the soil surface (0–10 cm). These values are suggested for the sandy oxisol soil as an environmental threshold for phosphorus.

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