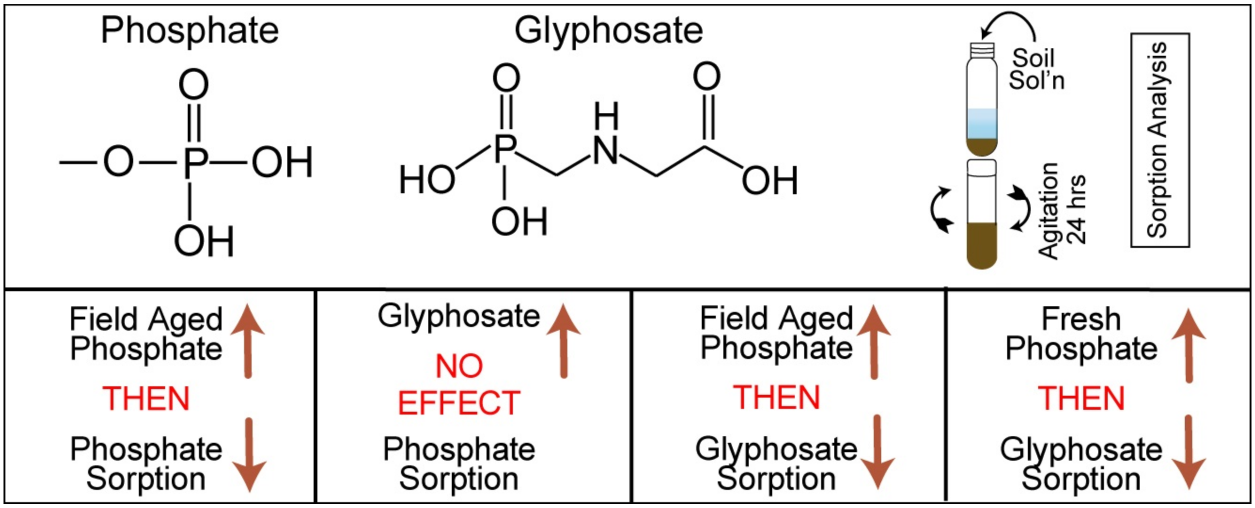
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Phosphate and glyphosate sorption in soils following long-term phosphate applications

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Abstract

Phosphate and glyphosate molecules compete for sorption sites in soil. The objective of this study was to quantify the impact of Olsen P concentrations in two contrasting soils on phosphate and glyphosate sorption. Soils were a sandy clay loam soil rich in iron oxides (SCL-Fe_2O_3) and a clay loam soil rich in calcium carbonates (CL-$CaCO_3$). The phosphate Freundlich sorption coefficient (K_f) ranged from 3 to 68 $L^{1/n}$ $mg^{1-1/n}$ kg^{-1} in the SCL-Fe_2O_3 and from 21 to 76 $L^{1/n}$ $mg^{1-1/n}$ kg^{-1} in the CL-$CaCO_3$. Glyphosate sorption coefficient (K_d) ranged from 293 to 1173 L kg^{-1} in the SCL-Fe_2O_3 but only 99 to 141 L kg^{-1} in the CL-$CaCO_3$. Glyphosate K_d and phosphate K_f values decreased significantly with increasing Olsen P concentrations in both soils. Glyphosate K_d values were further significantly reduced when phosphate was added to the slurry solutions, but phosphate K_f values were not impacted by the presence of glyphosate in solutions. We conclude that annual phosphate fertilizer applications leave phosphate concentrations in Prairie soils to the extent that soils have a lesser capacity to retain glyphosate and phosphate that are subsequently applied, but glyphosate residues will not influence phosphate sorption.

Keywords: Phosphate, Glyphosate, Olsen P, Batch equilibrium experiment, Freundlich sorption coefficient, Sorption coefficient, Prairie soil

1. Introduction

Sorption is an important process that influences the transport and availability of nutrients and pesticides in soil (Duke et al., 2012; Hiller et al., 2012; Ige et al., 2005). Phosphate is an essential nutrient for crop growth and annually applied to agricultural soils (Gomes et al., 2015). Glyphosate [*N*-(phosphonomethyl) glycine] is a broad spectrum, non-selective systemic herbicide and among the most widely used pesticides in the world (Duke and Powles, 2009; FOEE, 2013).

Amorphous Fe and Al oxides in soil are the preferred sorption sites for phosphate and glyphosate molecules (Barja and Afonso, 2005; Gimsing et al., 2004; Piccolo et al., 1994). Phosphate is preferentially sorbed by Fe-oxides because the phosphate molecule (0.25 nm) is smaller than the glyphosate molecule (0.43 nm) (Gimsing et al., 2007; Gimsing and Borggaard, 2001), but glyphosate is retained by Fe-oxides through both phosphonic acid and carboxylic acid moieties (Gimsing and Borggaard, 2001; Sprankle et al., 1975; Tévez and Afonso, 2015). Phosphate readily forms complexes with Ca^{2+} in calcareous soils (Busman et al., 2009) and glyphosate can form stable complexes with Ca^{2+} in solution and sorb (Glass, 1987) or form weak bonds with exchangeable Ca^{2+} associated with clays (de Jonge et al., 2001). Glyphosate can also be sorbed onto clay minerals (de Jonge et al., 2001), divalent cations of inter layer clay minerals (Piccolo et al., 1994) and organic matter (Morillo et al., 2000).

Sorption of phosphate and glyphosate by soil is typically determined using soil slurries in batch-equilibrium experiments (de Jonge et al., 2001; Gimsing et al., 2004; Gimsing and Borggaard, 2002; Ige et al., 2005). Phosphate and glyphosate molecules compete for sorption sites in soil and adding phosphate and glyphosate to soil slurries at the same time can influence sorption of the individual chemicals (de Jonge and de Jonge, 1999). For example, in a range of batch equilibrium studies, glyphosate sorption by soil was less when phosphate was added with glyphosate (Gimsing et al., 2007; Gimsing and Borggaard, 2007; Kanissery et al., 2015). Based on desorption experiments using batch equilibrium, two studies have shown that phosphate in soil has the potential to increase glyphosate desorption (Laitinen et al., 2008; Prata et al., 2003). In these studies, phosphate was applied to soil at 14 and 28 days prior to the start of batch equilibrium experiments, and glyphosate desorption increased by 1 to 13%, relative to soils that had not received phosphate. A recent study generated rainfall runoff at one day after glyphosate applications on a silty clay loam soil and showed that glyphosate concentrations in runoff were greater for plots that had also received phosphate applications (Sasal et al., 2015).

Recently, concerns have been raised about the possibility of glyphosate increasing the transport of phosphate to surface water thereby increasing the risk for lake eutrophication (Barrera, 2016). In batch equilibrium studies, when glyphosate was added at approximately 1000 to 1500 kg glyphosate ha^{-1} rate, glyphosate additions to soils were able to release some phosphate in acidic soil particularly in soils high in Al and Fe-oxides (Gimsing et al., 2004). Additions of the same amount of glyphosate as Gimsing et al. (2004), also released phosphate molecules bound to synthesized Al-oxides and but this release was not observed with synthesized Fe-oxides (Gimsing and Borggaard, 2002, 2001). Generally, farmers apply phosphate fertilizer at 20 to 40 kg P ha^{-1} and ~1 kg glyphosate ha^{-1} on their crop farms (Akinremi and Grant 2014; Benbrook, 2016). Thus, these previous studies showed that glyphosate has the potential to release phosphate but the concentrations of glyphosate used were much greater than environmentally relevant. It is unknown whether glyphosate can influence the retention of phosphate in calcarious soils. In our study, we utilized a soil high in Fe-oxides and a soil high in calcium carbonates and, for these soils, we were interested in testing whether there is any potential effect of glyphosate on phosphate sorption. Like previous studies that focused on acidic soils and Al and Fe-oxides (Gimsing et al., 2004; Gimsing and Borggaard, 2002, 2001), we utilized an amount of glyphosate that was much larger than relevant field doses.

Batch equilibrium studies of glyphosate or phosphate sorption typically use either 0.01M $CaCl_2$ or 0.01M KCl as background electrolyte solutions (Bhattacharyya et al., 2015; de Jonge et al., 2001; Gimsing and Borggaard, 2001; 2007; Okada et al., 2016). The batch equilibrium process does not distinguish between sorption and precipitation (Siebsen 1981; Akinremi, 1990; Muhammad, 1992). At pH 7, the background electrolyte solution strongly influenced the sorption of phosphate by Fe-oxides because with 0.01M $CaCl_2$, phosphate formed complexes with Ca^{2+} and precipitated, while this did not occur with 0.01M or 0.1M KCl (Gimsing and Borggaard, 2001). However, under the same conditions, the background electrolyte solution had little influence on glyphosate sorption by Fe-oxides (Gimsing and Borggaard, 2001).

Long-term phosphate fertilizer applications result in the build-up of phosphate in agricultural soils (de Jonge et al., 2001). Crops only utilize a small portion of the phosphate applied because sorption limits the availability of phosphate for plant uptake in soil (Holford, 1997). Long-term phosphate-fertilizer applications to sandy clay loam and loamy sand soils in India reduced the ability of the soils to retain phosphate molecules, as determined by batch equilibrium experiments (Bhattacharyya et al., 2015; Varinderpal-Singh et al., 2006). Long-term phosphate fertilizer applications to a sandy clay loam soil in Canada and coarse sand and sandy loam soils in Denmark resulted in fertilized soils showing significantly lesser glyphosate sorption than untreated soils, also as determined by batch equilibrium experiments (de Jonge et al., 2001; Munira et al., 2016; 2017). The combination of fresh phosphate applications to soils containing field-aged phosphate and the impact of these phosphate concentrations on glyphosate sorption has received no attention except for Munira et al. (2016).

It is unknown whether increasing field-aged-phosphate concentrations have the same impact on reducing phosphate sorption as they have on reducing glyphosate sorption. In this study, we used a soil high in Fe-oxides (pH 4.7 to 5) versus a soil high in calcium carbonates (pH 7.3 to 7.5) that were both subjected to long-term phosphate fertilizer applications at 20, 40 and 80 kg P ha^{-1} resulting in a range of Olsen P concentrations due to the build-up of phosphate in soil during eight years of annual applications. Using 0.01M KCl and 0.01M $CaCl_2$ as background electrolyte solutions, the objective of this study was to examine the impact of 1) field-aged phosphate concentrations and a commercially available glyphosate formulation on phosphate sorption in soils rich in iron oxides or calcium carbonates and 2) field-aged phosphate concentrations in combination with fresh phosphate on glyphosate sorption in these two contrasting soils.

2. Materials and Methods

2.1. Chemicals

Chemicals used were analytical grade glyphosate (99.9% purity) from Sigma-Aldrich Co., St. Louis, MO; [phosphonomethyl-^{14}C]glyphosate (99% radiochemical purity; specific activity 50 mCi/mmol) from American Radiolabeled Chemicals Inc., St. Louis, MO; Roundup Ultra2$^{®}$ (49%

active ingredient and 51% other ingredients, CAS No. 70901-12-1) from Monsanto Chemical Company; and analytical grade potassium dihydrogen phosphate (KH_2PO_4) (99% chemical purity), potassium chloride (100% chemical purity) and calcium chloride, dihydrate (>95% chemical purity) from Fisher Scientific, Fair Lawn, NJ.

2.2. Soil Characteristics and Experimental Design

This study utilized soil samples (0-15 cm) obtained from long-term experimental plots under a durum wheat and flax rotation near Carman (49° 29.7' N, 98° 2.4' W) and near Forrest (50° 1.2' N, 99° 53.3' W) Manitoba, Canada. Soil profiles at both sites were classified based on the Canadian System of Soil Classification as Orthic Black Chernozems, which is equivalent to the Udic Boroll subgroup in the U.S. Soil Taxonomy (Soil Classification Working Group, 1998). The experimental design at each site was a randomized complete block design with four mono ammonium phosphate fertilizer treatments and four replicates plots. Treatments were a control (no phosphate applications), and plots receiving annual applications of mono ammonium phosphate fertilizers at 20, 40, and 80 kg P ha^{-1}, (Grant et al., 2013) or 20P, 40P, and 80P, respectively, from 2002 to 2009. For all plots that received mono ammonium phosphate, 20 kg P ha^{-1} was placed near the seed to enhance fertilizer use efficiency, a common practice in Canadian Prairie agriculture. For the 40 and 80 kg P ha^{-1} treatments, to avoid seedling toxicity, the additional mono ammonium phosphate was broadcast and then incorporated. From 2010 to 2013, the rotation was continued but no phosphate was applied. Application of urea fertilizer differed by year. Generally, durum wheat received 90 kg N ha^{-1} and flax 50 kg N ha^{-1}.

From each plot, composite samples were collected in spring, 2013 using a Dutch auger with ten (Carman) to eight (Forrest) samples per plot and cleaning the auger between plots. Soil samples were air-dried and sieved (<2mm) prior to soil property analyses and sorption experiments. The Carman soil has a sandy clay loam texture and is relatively high in iron oxides (SCL-Fe_2O_3), whereas the Forrest soil has a clay loam texture and is relatively high in calcium carbonates (CL-$CaCO_3$) (Table 1). Available phosphate was extracted using the Olsen (0.5 M $NaHCO_3$, pH 8.5) phosphorus test. 2 g of air dried soil and 40 ml of 0.5N $NaHCO_3$ solution was mixed in a 50 mL Erlenmeyer flask. Flasks (duplicates) were shaken horizontally (200 excursions min^{-1}). Equilibrium solutions were filtered through Whatman No. 2 filter paper and phosphate concentrations were determined colorimetrically (Frank et al., 2011).

2.3. Phosphate Sorption

Phosphate sorption was determined by batch equilibrium using either 0.01M $CaCl_2$ or 0.01M KCl as the background electrolyte. Batch equilibrium procedures followed standard protocols using a soil/solution ratio of 1:10 and an equilibrium time of 24h (Ige et al., 2005). Two experiments were conducted utilizing soil samples: (1) from all plots at each site to quantify the effect of Olsen P concentrations on phosphate sorption in soil and (2) from control and 80P plots at each site to quantify the effect of Roundup Ultra2 additions to soil slurries on phosphate sorption in soil.

2.3.1. Effect of field-aged phosphate concentrations on sorption of phosphate

In the first experiment, potassium dihydrogen phosphate solutions (20 mL) at concentrations of 5, 10, 25, 50, 100, 150, 250 or 500 mg P L^{-1} were added to air-dried soil (2 g) in 50-mL centrifuge tubes (duplicates) and shaken horizontally (120 excursions min^{-1}) at room temperature (23±2°C) for 24h. Equilibrium solution was centrifuged (6,100 G for 10 min) and filtered (0.45 μm). Phosphate concentration was determined colorimetrically by the molybdate blue method (Murphy and Riley, 1962). Linearized Freundlich isotherm has been specified as: The phosphate sorption coefficient, K_f ($L^{1/n}$ $mg^{1-1/n}$ kg^{-1}), was calculated using the linearized form of Freundlich equation:

$\log q = \log K_f + 1/n \log C$

Where q represents phosphate sorption in soil at equilibrium (mg kg^{-1}), C represents phosphate concentration of equilibrium solution (mg L^{-1}), and 1/n represents the Freundlich slope. In addition, the Freundlich P sorption isotherm was used to determine the equilibrium P concentration (EPCo) at log q = 0, which is the concentration at which neither sorption nor desorption occurs and hence can be used to define whether a soil is likely to act as a sink (sorption) or source (desorption) of P (Indiati and Sharpley, 1998; Sharpley et al., 1994). EPCo levels above 0.025 mg L^{-1} (US EPA, 1988) suggest an increased risk of eutrophication because of P transport in soluble form.

2.3.2. Effect of glyphosate formulation on sorption of phosphate

In the second experiment, stock solutions of 150 mg P L^{-1} were prepared with and without 100 mg L^{-1} Roundup Ultra2 in the solution. The 100 mg L^{-1} Roundup Ultra 2 was equivalent to 378 mg glyphosate kg^{-1} soil. The 150 mg P L^{-1} solution was used because previous studies have proposed that this parameter (P150) is the most optimum single point in the isotherm reflective of the phosphate sorption capacity in soils (Ige et al., 2005). Batch equilibrium procedures were carried out as described above. The phosphate sorption coefficient, K_d (L kg^{-1}), was calculated by q/C, where q represents phosphate sorption by soil at equilibrium (mg kg^{-1}) and C represents phosphate concentration of equilibrium solution (mg L^{-1}).

2.4. Glyphosate Sorption

Glyphosate sorption was determined by batch equilibrium with the initial glyphosate solution containing 1 mg L^{-1} analytical-grade glyphosate and 6.67 X 10^4 Bq L^{-1} ^{14}C-labelled glyphosate. Two experiments were conducted utilizing soil samples: (1) from all plots to quantify at each site the effect of Olsen P concentrations on glyphosate sorption, and (2) from control and 80P plots to quantify at each site the effect of fresh phosphate additions to soil slurries on glyphosate sorption in soil.

2.4.1 Impact of field-aged phosphate concentrations on sorption of glyphosate

Batch equilibrium procedures followed the OECD guideline 106 using a soil/solution ratio of 1:5, an equilibrium time of 24h and 0.01M $CaCl_2$ or 0.01M KCl as background electrolyte (OECD, 2000). Glyphosate solutions (10 mL) were added to air-dried soil (2 g) in 50-mL centrifuge Teflon tubes (duplicates) and slurries were rotated in the dark at 5°C for 24h. Equilibrium solution was centrifuged (6,100 G for 10 min) and subsamples (1 mL) of supernatant were added in duplicated 7-mL scintillation vials containing 5 mL of 30% Scintisafe scintillation cocktail (Fisher Scientific, Fair Lawn, NJ). Radioactivity was quantified by Liquid Scintillation Counting (LSC) with automated quench correction (#H method) (LS 6500 Beckman Instruments, Fullerton, CA). The glyphosate sorption distribution constant, K_d (L kg^{-1}), was calculated by Cs/Ce, where Cs represents glyphosate sorption by soil at equilibrium (mg kg^{-1}) and Ce represents glyphosate concentration of equilibrium solution (mg L^{-1}). The difference between the added radioactivity and radioactivity in the supernatant was assumed to be the proportion of glyphosate having been sorbed.

2.4.2. Impact of fresh phosphate addition on sorption of glyphosate

Experiments followed similar batch equilibrium sorption protocols as described above. In this experiment, potassium dihydrogen phosphate was added to the initial glyphosate solution at rates equivalent to 11, 22 and 44 mg P kg^{-1} soil, or an estimated 20, 40 and 80 P kg ha^{-1}, respectively, when assuming the fertilizer being present in the top 15-cm layer of a soil with a bulk density of 1,200 kg m^{-3}.

2.5. Statistical analysis

Statistical analyses were carried out using SAS software version 9.3 for Windows (SAS Institute Inc. 2002-2010). Prior to each analysis, data sets were checked for outliers, normality of residuals and homogeneity of variances. Residuals were normally distributed and variances were homogeneous. The paired *t*-test ($P<0.05$) was used to test for the effect of background electrolyte solution (0.01M $CaCl_2$ versus 0.01M KCl) on glyphosate K_d or phosphate K_f and EPCo. For both background electrolyte solutions and at each site, simple linear regression analyses ($P<0.05$) were carried out to estimate glyphosate K_d and phosphate K_f values using Olsen P concentration as the independent variable. In each of the glyphosate K_d and phosphate K_f figures, the slopes of regression lines developed for SCL-Fe_2O_3 and CL-$CaCO_3$ were compared by including dummy variables in PROC REG to test whether the responses of sorption to increasing Olsen P concentrations was influenced by soil type. Simple linear regression analysis was also carried out to estimate glyphosate K_d values by using the added fresh phosphate concentration as an independent variable. The slopes of the regression lines developed for the 0P (control) and 80P plots in both soils were compared by including dummy variables in PROC REG to test whether the responses of sorption to increasing potassium dihydrogen phosphate concentration was influenced by Olsen P concentrations (0P, 80P). Simple linear regression analyses were carried out to determine the relationship between glyphosate K_d and phosphate K_f values by using K_f as an independent variable. Simple linear regression analyses ($P<0.05$) were also carried out to estimate EPCo values by using Olsen P as an independent variable for CL-$CaCO_3$ soil. Graphical plot fitting of EPCo as a function of Olsen P showed that data did not fit well with simple linear regression for the SCL-Fe_2O_3 soil. Therefore, data was fitted to an exponential non-linear model using PROC NONLIN. One-way ANOVA ($P<0.05$) was used to estimate the effect of Roundup Ultra2 on phosphate sorption in soils.

3. Results and discussion

3.1. Effect of background electrolyte solutions on sorption of phosphate and glyphosate

The types of ions in solution had a significant effect on phosphate and glyphosate sorption, except for glyphosate sorption in the CL-$CaCO_3$ soil (Table 2). Phosphate K_f values in both soils were significantly greater in experiments with 0.01M $CaCl_2$ than experiments with 0.01M KCl (Table 2). Phosphate K_f values were on average 54 $L^{1/n}$ mg $^{1-1/n}$ kg^{-1} in CL-$CaCO_3$ and 38 $L^{1/n}$ mg $^{1-1/n}$ kg^{-1} SCL-Fe_2O_3 with $CaCl_2$ but on average 36 $L^{1/n}$ mg $^{1-1/n}$ kg^{-1} in CL-$CaCO_3$ and 23 $L^{1/n}$ mg $^{1-1/n}$ kg^{-1} SCL-Fe_2O_3 with KCl. Thus, when 0.01M $CaCl_2$ was used with the SCL-Fe_2O_3 and CL-$CaCO_3$ soils but also when KCl was used with the CL-$CaCO_3$ soil, phosphate likely formed stable complexes with a portion of Ca^{2+} in soil solution and precipitated (Carreira et al., 2006; Devau et al., 2011; Gimsing and Borggaard, 2001). In batch equilibrium experiments with 0.01M $CaCl_2$, precipitation with Ca^{2+} occurs more readily for phosphate than glyphosate (Gimsing and Borggaard, 2001). For glyphosate sorption, K_d values were on average 116 L kg^{-1} in CL-$CaCO_3$ and 703 L kg^{-1} SCL-Fe_2O_3 with $CaCl_2$, and on average 117 L kg^{-1} in CL-$CaCO_3$ and 632 L kg^{-1} SCL-Fe_2O_3 with KCl. In calcareous soils, Ca^{2+} in forms a bridge between negatively charged soil colloids and glyphosate molecules in soil (Zhao et al., 2015) and, because of the already high free calcium content in the CL-$CaCO_3$ soil, the addition of Ca with 0.01M $CaCl_2$ solution had no impact on glyphosate sorption. For the SCL-Fe_2O_3 soil, glyphosate sorption was greater with 0.01M $CaCl_2$ than 0.01M KCl, suggesting that glyphosate was able to form complexes with Ca^{2+} in solution for enhanced sorption (Glass, 1987).

3.2. Effect of field-aged phosphate concentrations on sorption of phosphate

Despite being exposed to similar long-term phosphate fertilizer treatments, Olsen P ranged from 13 to 99 mg kg^{-1} in the acidic SCL-Fe_2O_3 soil but only from 8 to 48 mg kg^{-1} in the calcareous CL-$CaCO_3$ soil. Olsen P concentrations by treatment were on average 17 (control), 24 (20P), 44 (40P) and 89 (80P) mg kg^{-1} in the SCL-Fe_2O_3 soil and 13 (control), 18 (20P), 24 (40P) and 41 (80P) mg kg^{-1} in the CL-$CaCO_3$ soil. The Olsen P test was originally developed for calcareous soils and can overestimate plant available P in acidic soils (Kane et al., 2013), such as the SCL-Fe_2O_3. Olsen P measures the $NaHCO_3$ extractable phosphate in soil, but calcareous soil may also contain slow release inorganic phosphate (apatite minerals) extracted by 1M HCl (Cross and Schlesinger, 1995; Hedley et al., 1982; Yu et al., 2014). *Olsen P concentrations* ranged from 8 to 99 mg kg^{-1} in this research which is within the typical range of 8 to 114 mg kg^{-1} that has been reported for soils in North America (McDowell et al., 2001). Hence, the findings from this research on the sorption pattern of phosphate and glyphosate in soil would be applicable to a wider range of soils in North America.

Phosphate K_f values significantly decreased with the increasing concentrations of Olsen P in soil (Figure 1). The SCL-Fe_2O_3 and CL-$CaCO_3$ soils showed relatively similar phosphate sorption (Figure 1). Phosphate K_f values ranged from 3.2 to 68 $L^{1/n}$ mg $^{1-1/n}$ kg^{-1} in the SCL-Fe_2O_3 soil with 1/n values between 0.37 to 0.92, and from 21 to 76 $L^{1/n}$ mg $^{1-1/n}$ kg^{-1} in the CL-$CaCO_3$ soil with 1/n values between 0.68 to 0.92. These values are within the range of other studies (Bertrand et al., 2003; Jalali, 2007; Shafqat and Pierzynski, 2014). A maximum reduction of phosphate K_f value was observed in SCL-Fe_2O_3 soil. The phosphate K_f value in SCL-Fe_2O_3 was reduced by 95% in soil containing 99 mg kg^{-1} Olsen P relative to soil containing 13 mg kg^{-1} Olsen P. Thus, P accumulation in soil reduced the capacity of soil to hold P. Wang et al. (2015) also reported that sorption of P decreased with the increasing concentrations of Olsen P because long-term application of P fertilizer leads to the accumulation of P in soil. In their study, they showed that long-term (5 to 15 years) application of phosphate significantly reduced phosphate sorption by 56% in soil containing 53 mg kg^{-1} Olsen P relative to soil containing 15 mg kg^{-1} Olsen P.

Olsen P concentrations significantly predicted phosphate K_f (Figure 1) in both SCL-Fe_2O_3 and CL-$CaCO_3$. The effect of Olsen P concentrations on reducing phosphate sorption was more pronounced for SCL-Fe_2O_3 than CL-$CaCO_3$ (Table S5). For the phosphate K_f, the regression slopes were significantly different between the soils in case of 0.01M KCl but not with 0.01M $CaCl_2$ because the presence of Ca in solution led to the possibility of precipitation of phosphate-Ca^{2+} complexes in both soils (Busman et al., 2009; Carreira et al., 2006; Devau et al., 2011). Generally, in calcareous soil, Ca forms precipitation with the added phosphate in soil solution (Carreira et al., 2006). For 0.01M KCl, the CL-$CaCO_3$ showed a significantly steeper slope than SCL-Fe_2O_3 (Figure 1) because, with increasing Olsen P concentrations, more sorption sites remained available in SCL-Fe_2O_3. CL-$CaCO_3$ soil has less sorption sites available for the added phosphate than SCL-Fe_2O_3 soil because calcareous soils contain slow-release phosphate (e.g, octacalcium phosphate and apatite) which occupy sorption sites that otherwise would be available for the added phosphate (Cross and Schlesinger, 1995; Hedley et al., 1982; Shariatmadari et al., 2007).

EPCo significantly increased with increasing concentrations of Olsen P in both SCL-Fe_2O_3 and CL-$CaCO_3$ (Figure 2). EPCo values ranged from 0 to 0.281 mg L^{-1}, depending on the background electrolyte solution and soil (Figure 2). EPCo values in both soils were significantly greater in the experiments with 0.01M KCl than experiments with 0.01M $CaCl_2$ (Table 2) because of the formation of Ca^{2+}-phosphate complexes in both soils with 0.01M $CaCl_2$. All EPCo levels were below the threshold value of 0.025 mg L^{-1} (US EPA, 1988) except in the 80P plots. The average calculated EPCo values for the four replicated 80P plots was 0.031 mg L^{-1} for CL-$CaCO_3$ and 0.190 mg L^{-1} for SCL-Fe_2O_3 with 0.01M KCl, and 0.025 mg L^{-1} for SCL-Fe_2O_3 with 0.01M $CaCl_2$. Although this suggest that prairie soils have a low risk for soluble P transport, a recent review reported that a significant portion of phosphate in Prairie soils can be transported as dissolved P during snow melt runoff (Flaten, 2016). Phosphate can be transported from the agricultural soil when phosphate fertilizer is applied in excess of crop requirements (Kleinman et al., 2011) and also from plant residues during snow melt (Flaten, 2016).

3.3. Effect of glyphosate formulation on sorption of phosphate

Commercially available glyphosate formulation had no impact on phosphate sorption in soil because there were no significant differences in phosphate sorption between treatments with and without Roundup Ultra2 additions to soil slurries. Gimsing and Borggaard (2001) also found that, when glyphosate was added following phosphate additions to goethite, glyphosate did not displace the sorbed phosphate. In a recent article that was published in the magazine "No-Till Farmer" (Barrera 2016), a statement was made that "20-25 percent of the dissolved reactive phosphorus in runoff is caused by glyphosate [use]" because of the assumption that glyphosate residues in soil decreases phosphate retention in soil. However, in our batch-equilibrium study that utilized very high rates of Roundup Ultra2, there was no significant difference in phosphate sorption between treatments with and without Roundup Ultra2 additions to soil slurries. Thus, given our findings, the recent concerns stated in Barrera (2016) are unlikely to be applicable to the Prairie soils that were included in our studies.

3.4. Effect of field-aged phosphate on sorption of glyphosate

Glyphosate K_d values significantly decreased with the increasing concentrations of Olsen P in both SCL-Fe_2O_3 and CL-$CaCO_3$ (Figure 1). Glyphosate K_d values ranged from 293 to 1173 L kg^{-1} in the acidic SCL-Fe_2O_3 soil and from only 99 to 141 L kg^{-1} in the calcareous CL-$CaCO_3$ soil (Figure 1), and these values are within the range of other studies (Farenhorst et al., 2008; Kumari et al., 2016; Sørensen et al., 2006). Long-term application of phosphate fertilizer in soil reduced glyphosate sorption because pre-sorbed phosphate occupied the sorption sites that would otherwise be available to glyphosate (Gimsing et al., 2007). A maximum reduction in glyphosate K_d value was observed in SCL-Fe_2O_3 soil. The K_d value was reduced by 75% in soil containing 99 mg kg^{-1} Olsen P relative to soil containing 13 mg kg^{-1} Olsen P in SCL-Fe_2O_3. Thus, results indicate that glyphosate and phosphate compete for the same sorption sites in soil. Similar observations have been made by de Jonge et al. (2001) who reported that long-term (60 to 100 years) application of phosphate significantly reduced glyphosate sorption by 50% in soil containing 59 mg kg^{-1} Olsen P relative to soil containing 6 mg kg^{-1} Olsen P.

Olsen P concentrations significantly predicted glyphosate K_d (Figure 1) in both SCL-Fe_2O_3 and CL-$CaCO_3$. With both 0.01M $CaCl_2$ and 0.01M KCl, the slopes of the regressions predicting glyphosate K_d were significantly different between soils with the SCL-Fe_2O_3 showing steeper slopes than CL-$CaCO_3$ (Figure 1). Regardless of the solution used, the sorption of glyphosate was greater in SCL-Fe_2O_3 than CL-$CaCO_3$ because of the importance of Fe_2O_3 in providing sorption sites for the negatively charged glyphosate in acidic soils. Research findings indicate that the presence of iron-oxide and soil pH had a stronger influence on glyphosate than phosphate sorption (Gimsing et al., 2004). The SCL-Fe_2O_3 soil contained 94% more Fe-oxides and 83% more Al-oxides than the CL-$CaCO_3$ soil (Table 1), and glyphosate sorption was greater in SCL-Fe_2O_3 soil because glyphosate sorption has been shown to be positively correlated with Fe/Al-oxides (Gimsing et al., 2004; Ololade et al., 2014). In addition, glyphosate sorption was greater in SCL-Fe_2O_3 (pH 4.7 to 5) than CL-$CaCO_3$ (pH 7.3 to 7.5) soil because glyphosate sorption is negatively correlated with soil pH (Gimsing et al., 2004). This is because with increasing soil pH, an increasing portion of the glyphosate molecules become negatively charged with glyphosate molecules existing as HG^{2-} (~100%) (net negative charge of glyphosate is 2^-) at pH 7.3-7.5 (Yu-jun et al., 2004), and soil colloid deprotonation increases (McConnell and Hossner, 1985) with soil colloids having a net negative charge in Prairie soils when soil pH > 6 (Lavkulich and Arocena, 2011). Hence, regardless of the background electrolyte solutions, the sorption of glyphosate was always relatively low in the CL-$CaCO_3$ soil (Figure 1). Thus, the effect of Olsen P concentrations on reducing glyphosate sorption was more pronounced for SCL-Fe_2O_3 than CL-$CaCO_3$ (Table S5). For example, with 0.01M KCl, glyphosate K_d was reduced by 39% when the phosphate concentration increased from 17 mg kg^{-1} (control) to 44 mg kg^{-1} (40P plots) in SCL-Fe_2O_3 but by only 11% when the phosphate concentration increased from 13 mg kg^{-1} (control) to 41 mg kg^{-1} (80P plots) in CL-$CaCO_3$ (Table S5).

3.5. Association between glyphosate K_d and phosphate K_f in relation to field-aged phosphate

Phosphate K_f and glyphosate K_d values were positively correlated (Figure 3). Thus, agreeing with previous studies suggesting phosphate and glyphosate have similar sorption pattern in soil (Barja and Afonso, 2005; Gimsing et al., 2007). However, regardless of the background electrolyte solution, phosphate K_f and glyphosate K_d were more strongly correlated in SCL-Fe_2O_3 than CL-$CaCO_3$ (Table S3). Hence, glyphosate and phosphate may compete more strongly for sorption sites in acidic soils with high Fe/Al-oxides content than in calcareous soils. In both soils and under both electrolyte background solutions, phosphate sorption was more strongly reduced by Olsen P concentrations than glyphosate sorption was reduced by Olsen P concentrations (Table S5). Thus, long-term application of phosphate fertilizer has an overall greater impact on reducing phosphate sorption than glyphosate sorption.

3.6. Effect of fresh phosphate addition on the sorption of glyphosate

Regardless of the background electrolyte solution and soil, the potassium dihydrogen phosphate additions to soil slurries significantly decreased glyphosate K_d values (Figure 4). Addition of fresh phosphate significantly reduced glyphosate sorption because the chemicals competed for the same sorption sites as they have similar phosphonate functional groups (Gimsing and Borggaard, 2001; Sprankle et al., 1975). Gimsing and Borggaard, (2002) studied the competitive sorption effect of fresh phosphate on glyphosate in soil and concluded that phosphate is preferentially sorbed over glyphosate. In addition to this, sorption of phosphate lowers the zero point charge of sorption sites such as Fe/Al-oxides, potentially increases the net negative charge on the oxide surfaces and thereby increasing the electrostatic repulsion between glyphosate and soil oxides (Gimsing et al., 2007).

Fresh phosphate significantly predicted glyphosate K_d (Figure 4) in both SCL-Fe_2O_3 and CL-$CaCO_3$. The regression slope was significantly steeper for 0P plots (control) than 80P plots in both soils and regardless of the background electrolyte solution (Figure 4). Thus, the effect of potassium dihydrogen phosphate addition in reducing glyphosate K_d values was less in soils that had greater Olsen P concentrations because less sorption sites were available for the added phosphate to compete with glyphosate molecules. This impact of phosphate already in soil was larger in SCL-Fe_2O_3 than CL-$CaCO_3$ (Table S6) because in CL-$CaCO_3$ soil at pH 7.3-7.5, glyphosate molecule existed as HG^{2-} (~100%) (Yu-jun et al., 2004) leading to less sorption, both in the presence and absence of fresh phosphate (Table S6). Thus, the competitive effect of phosphate on glyphosate is stronger in soils that are acidic and contain substantial amount of Fe-oxides than in calcareous soils.

4. Conclusion

The sorption of phosphate and glyphosate was reduced due to the long-term addition of phosphate fertilizer in two Prairie soils. The impact of Olsen P on reducing glyphosate sorption was more pronounced in the acidic (iron-oxide rich) sandy clay loam than the calcareous (calcium carbonate rich) clay loam soil, both with or without the addition of potassium dihydrogen phosphate. Regardless of the background electrolyte and soil type, phosphate sorption was more strongly reduced by the Olsen P concentrations than glyphosate sorption. The reduction of glyphosate sorption due to the application of potassium dihydrogen phosphate was greater in soils containing low Olsen P concentrations. The equilibrium phosphate concentration was above the threshold level for eutrophication only in soils that had exceptionally high phosphate concentrations i.e., the soils had received annual applications of mono ammonium phosphate at rates of 80 kg ha^{-1} for eight years. Commercially formulated glyphosate had no influence on phosphate sorption suggesting that glyphosate residues in soils have no impact on phosphate sorption or mobility.

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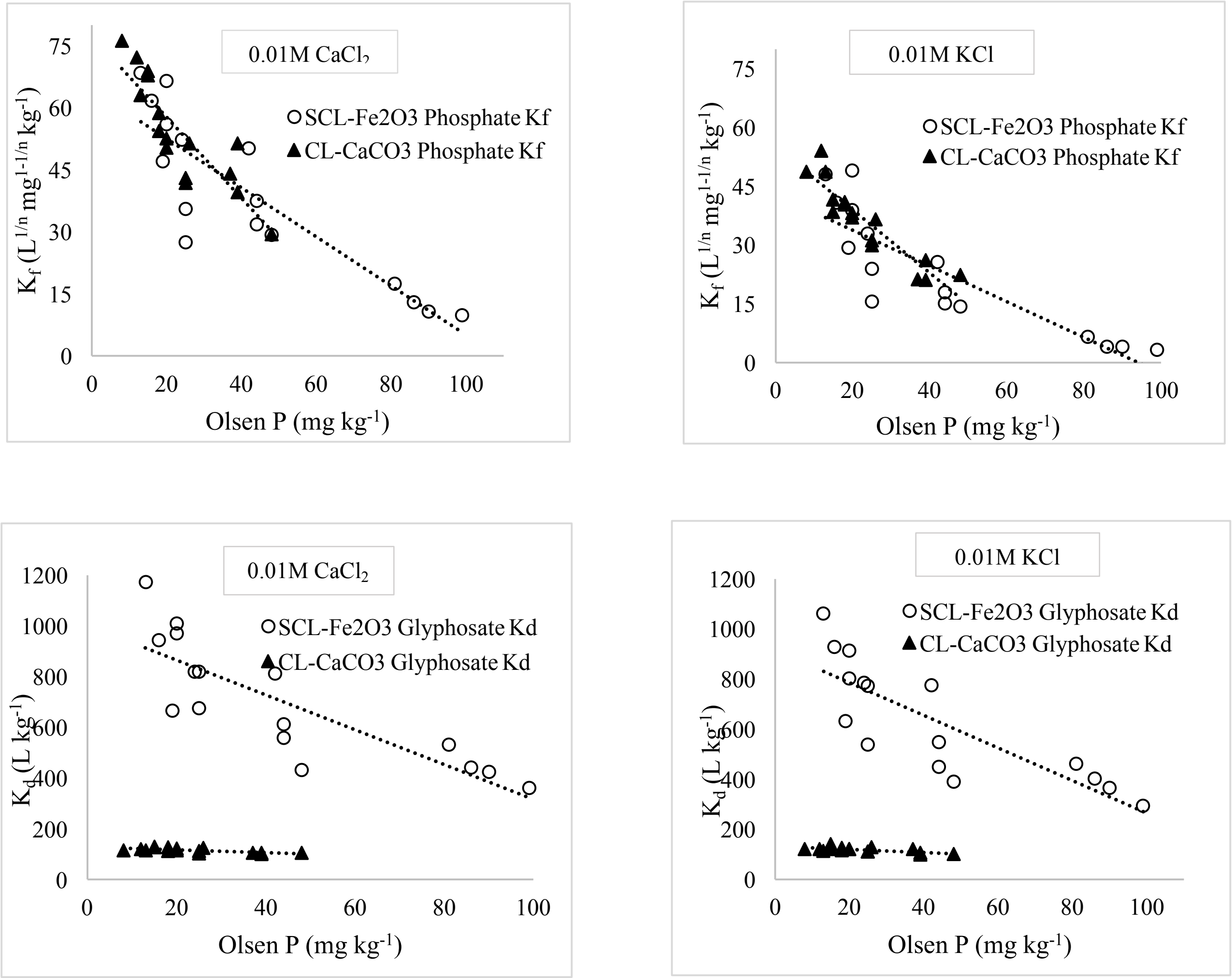
Figure Captions

Figure 1. Effect of Olsen P concentrations in soil on glyphosate and phosphate sorption in SCL-Fe_2O_3 and CL-$CaCO_3$ soils, as determined by batch equilibrium experiments using 0.01M $CaCl_2$ or 0.01M KCl as background electrolyte solutions. All regression equations are significant at $P<0.05$ and the equations are given in Table S1-Supplementary information.

Figure 2. Effect of Olsen P concentrations in soil on the phosphate equilibrium concentration, (EPCo) in SCL-Fe_2O_3 and CL-$CaCO_3$ soils determined by batch equilibrium experiments using 0.01M $CaCl_2$ or 0.01M KCl as background electrolyte solutions. Olsen P All regression equations are significant at $P<0.05$ and the equations are given in Table S1, S2-Supplementary information.

Figure 3. Association between glyphosate K_d and Phosphate K_f in SCL-Fe_2O_3 and CL-$CaCO_3$ soils with sorption being determined by batch equilibrium experiments using 0.01M $CaCl_2$ or 0.01M KCl as background electrolyte solutions. All regression equations are significant at $P<0.05$ and the equations are given in Table S3-Supplementary information.

Figure 4. Effect of potassium dihydrogen phosphate concentrations on glyphosate sorption in SCL-Fe_2O_3 and CL-$CaCO_3$ soils with low (0P) or high (80P) Olsen P concentrations. Potassium dihydrogen phosphate was added to glyphosate in soil sluries during batch equilibrium experiments using 0.01M $CaCl_2$ and 0.01M KCl. All regression equations are significant at $P<0.05$ and the equations are given in Table S4-Supplementary information. The values in parentheses in each legend represent mean values of Olsen P and standard error.



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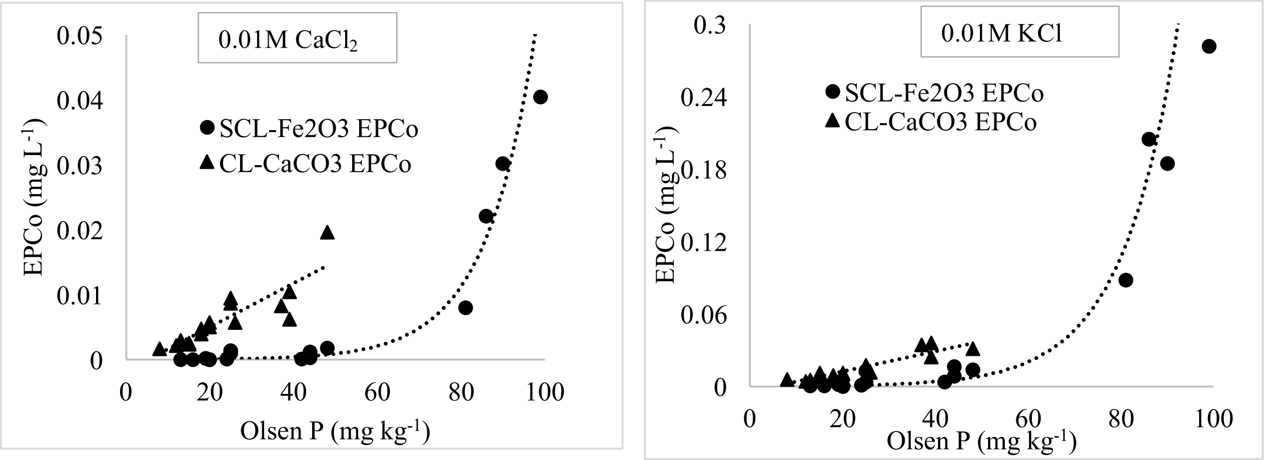

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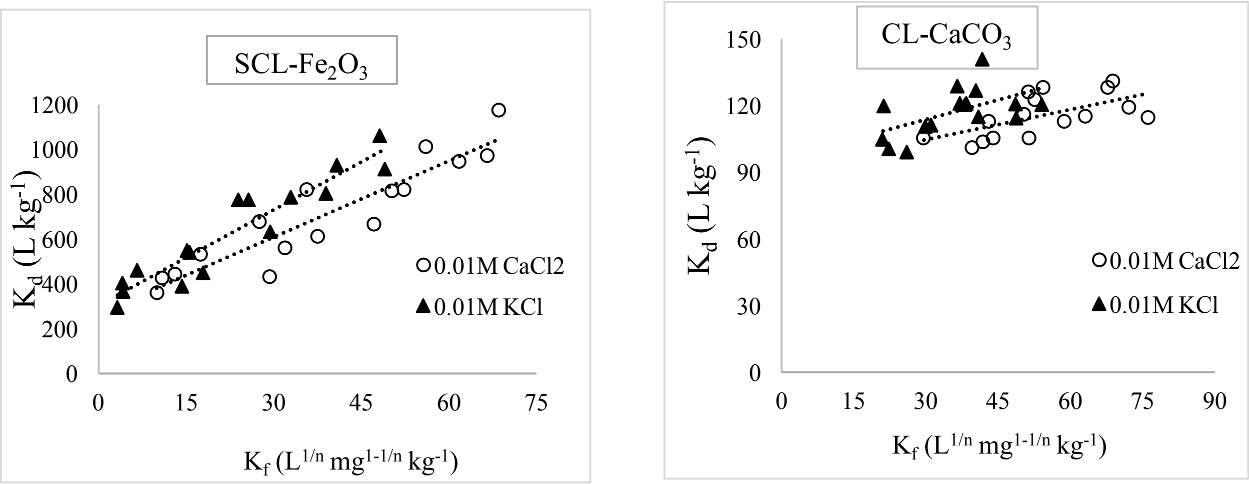

Figure 3. Association between glyphosate K_d and Phosphate K_f in SCL-Fe_2O_3 and CL-$CaCO_3$ soils with sorption being determined by batch equilibrium experiments using 0.01M $CaCl_2$ or 0.01M KCl as background electrolyte solutions. All regression equations are significant at $P<0.05$ and the equations are given in Table S3-Supplementary information.

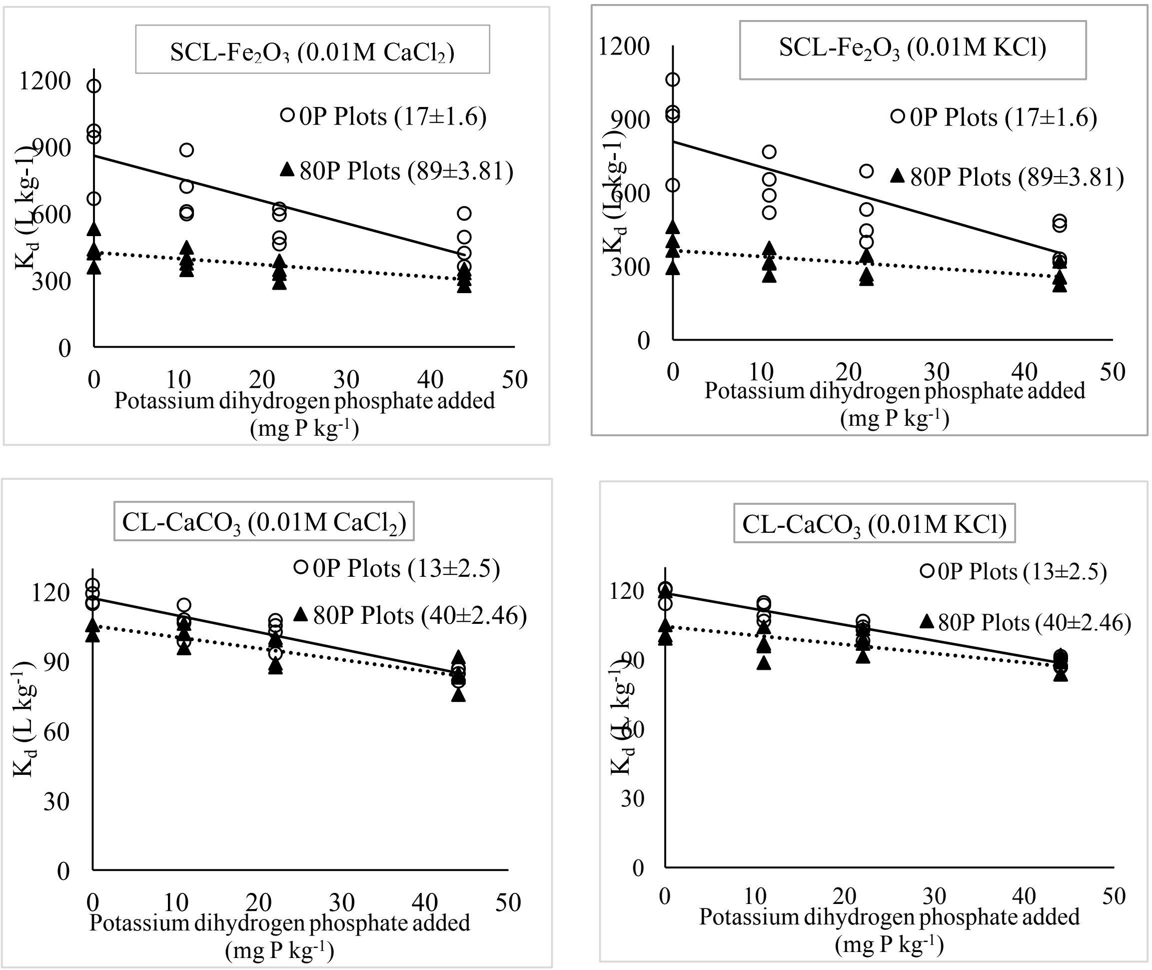

Figure 4. Effect of potassium dihydrogen phosphate concentrations on glyphosate sorption in SCL-Fe_2O_3 and CL-$CaCO_3$ soils with low (0P) or high (80P) Olsen P concentrations. Potassium dihydrogen phosphate was added to glyphosate in soil sluries during batch equilibrium experiments using 0.01M $CaCl_2$ and 0.01M KCl. All regression equations are significant at $P<0.05$ and the equations are given in Table S4-Supplementary information. The values in parentheses in each legend represent mean values of Olsen P and standard error.

Table 1. Selected soil physical and chemical properties as mean with standard error

Soil	Organic Carbon [a] (%)	pH[b]	Fe_2O_3[c] (mg kg^{-1})	Al_2O_3[c] (mg kg^{-1})	Ca[d] (mg kg^{-1})	Clay[e] %	Silt[e] %	Sand[e] %
SCL-Fe_2O_3	2.81 ± 0.04	4.7± 0.02	237±7.93	6.41±0.64	2252±35	20	20	60
CL-$CaCO_3$	3.2 ± 0.07	7.3± 0.02	12.52±0.22	1.07±0.47	4791±158	30	39	31

[a] Soil organic carbon content was determined using combustion technique with a high temperature induction furnace (Nelson and Somemers, 1996). [b] Soil pH was determined using a 10 ml 0.01M $CaCl_2$ solution and 2 g soil solution ratio (Jones Jr, 2001). [c] Extractable Fe and Al were extracted with diethylenetriaminepentaacetic acid *(DTPA)* (Whitney, 2011) and 0.01M $CaCl_2$, (Barnhisel and Bertsch, 1982) respectively, and extracts were analyzed by *ICP*. [d] Extractable Ca was also measured by *ICP* using ammonium acetate as an extractant (Warncke and Brown, 2011) [e] data adapted Grant et al., (2013).

Table 2. Statistical parameters (Paired t-tests) on the effect of background electrolyte solution (0.01M $CaCl_2$ versus 0.01M KCl) on glyphosate (L kg^{-1}) and phosphate sorption coefficient (L$^{1/n}$ mg $^{1-1/n}$ kg^{-1}) in soils.

Sorption Parameter	Soil	Mean		DF	t Value	Pr > |t|
		0.01M $CaCl_2$	0.01M KCl			
Phosphate sorption coefficient, K_f	SCL-Fe_2O_3	38.47	23.11	15	11.14	<.0001
	CL-$CaCO_3$	54.08	36.04	15	10.94	<.0001
Glyphosate sorption coefficient, K_d	SCL-Fe_2O_3	703	632	15	5.89	<0.0001
	CL-$CaCO_3$	116	117	15	-1.55	0.1430
Phosphate Equilibrium Concentration, EPCo	SCL-Fe_2O_3	0.007	0.04	15	-2.29	<.0366
	CL-$CaCO_3$	0.006	0.015	15	-4.72	<.0003

Supplementary Information

Supplementary Information Available: Tables S1, S2, S3, S4, S5, and S6 containing linear and non-linear regression equations to predict phosphate K_f and glyphosate K_d

Table S1. Simple linear regression results using Olsen P as independent variables to predict phosphate, glyphosate sorption coefficient and phosphate equilibrium concentration in SCL-Fe_2O_3 and CL-$CaCO_3$ soils except phosphate equilibrium concentration in SCL-Fe_2O_3 soil was non-linear

Parameter	Soil	Electrolytes	Linear Model	R^2	P value
Phosphate Kf	SCL-Fe_2O_3	0.01M $CaCl_2$	K_f = - 0.59 Olsen P + 64.19	0.75	***
		0.01M KCl	K_f = - 0.46 Olsen P + 42.10	0.75	***
	CL-$CaCO_3$	0.01M $CaCl_2$	K_f = - 0.98 Olsen P + 77.17	0.77	***
		0.01M KCl	K_f = - 0.81 Olsen P + 55.08	0.85	***
Glyphosate Kd	SCL-Fe_2O_3	0.01M $CaCl_2$	K_d = - 6.85 Olsen P + 1001	0.69	***
		0.01M KCl	K_d = - 6.53 Olsen P + 916.07	0.67	***
	CL-$CaCO_3$	0.01M $CaCl_2$	K_d = - 0.55 Olsen P + 128.63	0.43	**
		0.01M KCl	K_d = - 0.60 Olsen P + 131.48	0.42	**
Phosphate EPCo	CL-$CaCO_3$	0.01M $CaCl_2$	EPCo = 0.0003 Olsen P – 0.0017	0.75	***
		0.01M KCl	EPCo = 0.0008 Olsen P – 0.0047	0.86	***

, and * denotes level of significance; p<0.01, and p<0.0001, respectively

Table S2: Parameters for the non-linear exponential model to predict phosphate equilibrium concentration using Olsen P as independent variable in SCL-Fe_2O_3 soil

Electrolytes	Non-linear model	P value
0.01M $CaCl_2$	$EPCo = 0.0001e^{0.06 \text{Olsen P}}$	***
0.01M KCl	$EPCo = 0.0002e^{0.05 \text{Olsen P}}$	***

*** denotes level of significance; p<0.0001

Table S3. Simple linear regression results using phosphate sorption coefficient K_f to predict glyphosate sorption distribution coefficient Kd in SCL-Fe_2O_3 and CL-$CaCO_3$ soils.

Soil	Electrolytes	Linear Model	R^2	P value
SCL-Fe_2O_3	0.01M $CaCl_2$	$K_d = 11.34 K_f + 267.30$	0.85	***
	0.01M KCl	$K_d = 14.19 K_f + 303.83$	0.89	***
CL-$CaCO_3$	0.01M $CaCl_2$	$K_d = 0.45 K_f + 91.12$	0.37	*
	0.01M KCl	$K_d = 0.58 K_f + 96.43$	0.30	*

*, **, and *** denotes level of significance; $p<0.05$, $p<0.01$, and $p<0.0001$, respectively

Table S4. Simple linear regression results using potassium dihydrogen phosphate as independent variables to predict glyphosate sorption coefficient K_d (L kg^{-1}) SCL-Fe_2O_3 and CL-$CaCO_3$ soils

Soil	Plots	Electrolytes	Linear Model	R^2	P value
SCL-Fe_2O_3	0P	0.01M $CaCl_2$	K_d = - 10.12 Fresh P + 859	0.58	**
		0.01M KCl	K_d = - 10.30 Fresh P + 805	0.63	**
	80P	0.01M $CaCl_2$	K_d = - 2.73 Fresh P + 425	0.50	**
		0.01M KCl	K_d = - 2.42 Fresh P + 362	0.40	**
CL-$CaCO_3$	0P	0.01M $CaCl_2$	K_d = - 0.73 Fresh P + 116.96	0.87	***
		0.01M KCl	K_d = - 0.63 Fresh P + 118.64	0.94	***
	80P	0.01M $CaCl_2$	K_d = - 0.49 Fresh P + 105.27	0.74	***
		0.01M KCl	K_d = -0.39 Fresh P + 104.39	0.53	**

, and * denotes level of significance; $p<0.01$, and $p<0.0001$, respectively

Table S5. Effect of Olsen P concentrations on reducing phosphate (K_f) or glyphosate (K_d) sorption relatively to control plots in SCL-Fe_2O_3 and CL-$CaCO_3$ soils, and on the equilibrium phosphate concentration (EPCo) values in SCL-Fe_2O_3 and CL-$CaCO_3$ soils.

Background Electrolyte Solution	Treatment	Reduction of K_f (%)		Reduction of K_d (%)	
		SCL-Fe_2O_3	CL-$CaCO_3$	SCL-Fe_2O_3	CL-$CaCO_3$
0.01M KCl	Control	-	-	-	-
	20P	33	16	18	0
	40P	56	28	39	1
	80P	89	52	57	11
0.01M $CaCl_2$	Control	-	-	-	-
	20P	30	13	13	0
	40P	39	22	36	0
	80P	79	38	53	11

Table S6. Effect of potassium dihydrogen phosphate reducing glyphosate sorption (K_d) in SCL-Fe_2O_3 and CL-$CaCO_3$ soils, with sorption being determined by batch equilibrium experiments using 0.01M $CaCl_2$ or 0.01M KCl as background electrolyte solutions.

Solution	Treatment (mg L^{-1})	Reduction of K_d (%)		Reduction of K_d (%)	
		SCL- Fe_2O_3		CL-$CaCO_3$	
		0P	80P	0P	80P
0.01M KCl	0	-	-	-	-
	11	29	17	7	9
	22	42	21	14	8
	44	54	31	25	18
0.01M $CaCl_2$	0	-	-	-	-
	11	25	10	9	3
	22	42	23	13	10
	44	50	28	28	20