Journal of Environmental Quality TECHNICAL REPORTS

VADOSE ZONE PROCESSES AND CHEMICAL TRANSPORT

Interactions among Glyphosate and Phosphate in Soils: Laboratory Retention and Transport Studies

Joshua T. Padilla* and H. Magdi Selim

Abstract

The purpose of this study was to determine the effect of PO_4 on the sorption and transport of glyphosate [*N*-(phosphonomethyl) glycine, GPS] in soils. The results of batch experiments indicated significant competition between PO_4 and GPS in two different soils, with PO_4 being preferentially sorbed. The 24-h Freundlich partitioning coefficients for GPS sorption were decreased by 50 to 60% with PO_4 in solution. High sorptive capacities exhibited by soils in the presence of PO_4 suggest the existence of both competitive and ion specific sites in either soil. Miscible displacement transport studies indicated limited effects of competition when GPS was applied in conjunction with or subsequent to pulses of PO_4. However, when a PO_4 pulse was applied after the application of a GPS pulse, a secondary GPS breakthrough was observed where an additional 4% of the applied herbicide mass was recovered in the effluent solution. This is likely attributed to the PO_4–mediated displacement of GPS bound to competitive sites. These results are further emphasized by the distribution of residual herbicide in this column, with enrichment of mass at lower depths in the column and a corresponding decrease in GPS mass closer to the column surface. These results indicate that the timing of inorganic P fertilizers relative to GPS applications has a significant impact on the fate of the herbicide in soils. In particular, these findings suggest that GPS may be more liable to leaching in scenarios in which P fertilizers are applied after the application of GPS-based herbicidal formulations.

Core Ideas

- Sorption of glyphosate by soils is decreased in the presence of phosphate.
- Phosphate can displace soil-bound glyphosate.
- Timing of phosphate application affects the mobility and fate of glyphosate in soils.

J. Environ. Qual. 48:156–163 (2019)
doi:10.2134/jeq2018.06.0252
Supplemental material is available online for this article.
Received 6 July 2018.
Accepted 21 Sept. 2018.

*Corresponding author (jpadilla@agcenter.lsu.edu).

PHOSPHORUS is an essential plant nutrient, and thus agricultural soils are often supplemented with additional P via fertilizer application. Glyphosate [*N*-(phosphonomethyl) glycine, GPS] is currently the most widely used herbicide in the United States and throughout the world. Benbrook (2016) estimates that >113 million kg of the herbicide was applied in agricultural settings in the United States during 2014, and that nearly 747 million kg was applied globally the same year. Therefore, it is expected that the coexistence of GPS and inorganic forms of P (PO_4^{3-}) in agricultural soils is pervasive. Since the introduction of GPS-based herbicidal formulations, it has been acknowledged that competitive interactions between the two chemicals at the mineral surface may be significant due to the considerable molecular similarity between PO_4^{3-} and the highly reactive phosphonomethyl functional group of the GPS molecule (Sprankle et al., 1975). As such, substantial effort has been put forth to investigate the behavior of the chemicals in soils when they are simultaneously present.

Typical ranges of GPS and PO_4 in soils are highly dependent on soil type and land use management. Maximum levels of GPS in soils from agriculturally intensive areas of Argentina range from 1.2 to 8.1 mg kg^{-1} soil (Primost et al., 2017; Okada et al., 2018), whereas total soil P typically ranges from 10^1 to 10^3 g P kg^{-1} soil (Kruse et al., 2015). Several studies demonstrated that GPS sorption by soils decreased in the presence of PO_4. Studying the effect of field-aged P on GPS sorption, de Jonge et al. (2001) reported reductions of Freundlich partitioning coefficients as much as 50% in soils with the greatest contents of Olsen P, relative to soils with the lowest concentrations of Olsen P. A similar finding was reported by Munira et al. (2016) where linear partitioning coefficients were reduced by 25 to 44% in soils with high concentrations of Olsen P relative to control soils, consistent with findings from a more recent study (Munira et al., 2018). Additionally, Kanissery et al. (2015) found that GPS sorption was significantly decreased by PO_4 addition under both oxic and anoxic conditions.

While investigating competitive interactions between GPS and PO_4 at the mineral surface of goethite, Gimsing and Borggaard (2001) concluded that PO_4 can displace already sorbed GPS; however, GPS did not demonstrate an ability to

---

School of Plant, Environmental and Soil Science, Louisiana State Univ., Baton Rouge, LA, 70803. Assigned to Associate Editor Wei Zheng.

Abbreviations: AMPA, aminomethylphosphonic acid; BTC, breakthrough curve; COM, center of mass; GPS, glyphosate; ICP–AES, inductively coupled plasma atomic emission spectroscopy; LSC, liquid scintillation counting; UPLC–MS/MS, ultra-performance liquid chromatography–tandem mass spectrometry.

desorb PO_4. The authors attributed this to desorption of GPS molecules bound to the surface via the carboxylic acid moiety, which is a binding mechanism confirmed in an atomic force microscopy study performed by Dideriksen and Stipp (2003). This is similar to the PO_4–mediated displacement of other carboxylic acids from goethite reported previously (Geelhoed et al., 1998). Extending this work to competitive interactions in mineralogically heterogeneous soils, Gimsing et al. (2004a) demonstrated that PO_4 can displace previously adsorbed GPS to a greater extent than PO_4 displacement by GPS additions. Here, competition was less pronounced than in pure mineral systems, and sorption seemed to occur on both competitive and ion-specific sites (additive sorption). This was a trend also evident in variably charged tropical soils (Gimsing et al., 2007). To further quantify this phenomenon, Gimsing et al. (2004b) described sorption kinetics with different models that accounted for both competitive and additive sorption, along with reversible and irreversible reactions. Gimsing et al. (2004b) also applied models that consider only competitive interactions between GPS and PO_4 and presented a description of data obtained from pure oxide mineral systems.

Displacement of previously soil-bound GPS is not without consequence in agricultural settings. Glyphosate residues mobilized by PO_4 fertilizer applications have been demonstrated to cause phytotoxic effects in tomatoes (*Solanum lycopersicum* L.; Cornish, 1992) and soybeans [*Glycine max* (L.) Merr.; Bott et al., 2011], and may have negative impacts on the function of vegetative buffer strips (Gomes et al., 2015). Gomes et al. (2016) reported enhanced root uptake of GPS in willow (*Salix* spp.) by PO_4 application, although phytotoxic effects may be minimized due to increased antioxidant activity attributed to greater plant P assimilation.

Although much of the work on GPS–PO_4 interactions has been limited to batch methods, results of transport studies may be more applicable to actual field conditions. Conducting column experiments involving soils with antecedent concentrations of P, Barrett and McBride (2007) reported an inability of GPS to mobilize PO_4 in coarse-textured soils but observed enhanced PO_4 mobility by GPS application in forest and dairy soils. Because PO_4 leaching was induced under GPS application rates greater than recommended agronomic rates, the authors concluded that there is only limited competition between GPS and PO_4 for sorption sites. Contrary to the results of enhanced mobility due to the presence of PO_4 from batch studies, Zhao et al. (2009) reported greater GPS retention in columns amended with PO_4 in two of three soils studied. As GPS is a polyprotic acid with four pKa values, the molecule has a propensity to protonate at lower pH values and therefore sorbs to soil surfaces more readily due to decreased repulsive forces between GPS and negatively charged clay minerals. Phosphate, added in the form of KH_2PO_4, induces a decrease in system pH. It would seem that in this situation, enhanced sorption brought about by a pH decrease overcomes any potential competitive effects of PO_4. Furthermore, Lu et al. (2005) concluded that enhanced mobility of GPS by PO_4 competition is dependent on soil type, where GPS mobility was increased in a red-paddy soil, and its retention was increased in sandy soil. Besides the above referenced studies, a literature search reveals that transport studies involving both GPS and PO_4 are lacking.

The objectives of this study were (i) to quantify the effect of PO_4 on the sorption and desorption of GPS by two Louisiana agricultural soils, (ii) to determine the effect of PO_4 on GPS mobility in soils, and (iii) to determine the effect of the timing of applications of GPS and PO_4 solutions (concurrent and consecutive GPS and PO_4 pulse applications) on the mobility of the herbicide in soil columns.

Materials and Methods

Soils

In this study, experiments were performed on two agricultural soils with varying physiochemical properties and no prior application history of GPS. The first soil, Commerce silt loam, is a fine silty, mixed superactive, thermic Fluvaquentic Endoaquept formed from alluvial deposits on the flood plains of the Mississippi River in the southeastern United States. Soil specifically used in this study was sampled from the surface horizon (0–5 cm) from the Louisiana State University AgCenter Sugarcane Research Station located in St. Gabriel, LA (19 km south of Baton Rouge). The second soil used in the experiments was Sharkey clay sampled from the surface horizon (0–5 cm) near Iberville Parish, LA, and is classified as a very fine, smectitic, thermic Chromic Epiaquert. The Commerce and Sharkey soils were collected in 2014 and 2013, respectively. Upon sampling, soils were air dried and made to pass through 2-mm sieves. All air-dried, sieved soil was stored in airtight plastic containers at ambient room temperatures prior to experiments. Select physiochemical properties of both soils are given in Supplemental Table S1.

Glyphosate Sorption and Desorption in the Presence of Phosphate

The quantification of the sorption and desorption of GPS from soils in the presence of PO_4 was performed following the batch technique discussed by Selim (2014). Glyphosate solutions at 1, 2, 5, 10, and 20 mg L^{-1} were prepared in background solution consisting of 5 mM KCl and 50-mg L^{-1} PO_4 (KH_2PO_4 at 71.65 mg L^{-1}), and spiked with ^{14}C-labeled GPS (phosphonomethyl group) such that initial radioactivity of each solution was $\sim 1.67 \times 10^2$ Bq mL^{-1}. Radiolabeled GPS was purchased from American Radiolabeled Chemicals, St. Louis, MO. Two grams of soil were weighed into 40-mL conical-bottom Teflon tubes, whereupon 20 mL of GPS solution at each input concentration was added. Each initial input concentration treatment was repeated in duplicate. A soil-free control, in which 30 mL of a 20-mg L^{-1} GPS solution was shaken for 24 h in a Teflon tube, demonstrated that GPS did not bind to the centrifuge tubes used in this study. Mixtures were then individually vortexed for 10 s to ensure homogenized suspensions, immediately transferred to a platform shaker, and continuously shaken at a constant temperature (21 ± 1°C) throughout the duration of the study. Solutions were sampled after 24 and 192 h of reaction time. It was determined in a separate study that 192 h was sufficient for equilibrium conditions to be obtained. This was performed by centrifuging tubes at 5000 rpm for 10 min and then transferring a 1-mL aliquot of the supernatant to a 7-mL scintillation vial. Four milliliters of scintillation cocktail (Packard Ultima Gold) was added to the vial, and mixtures were vortexed until homogenized. Samples were analyzed on a liquid scintillation counter (LSC, PerkinElmer TriCarb 4810 TR) using

5-min count times. No quench correction was made, and radioactivity was recorded as counts per minute. Glyphosate concentrations were determined by the relative radioactivity of the sample to that of the input solution.

Desorption commenced immediately after the 192-h sampling. This was performed by centrifuging tubes and decanting the entirety of the supernatant solution, which was then replaced with GPS-free 5 mM KCl and 50-mg L^{-1} PO_4 solution. Mixtures were vortexed and returned to the platform shaker for an additional 24 h, after which supernatant solutions were sampled as above. This was repeated an additional time for a total of two desorption steps. The extent of desorption was determined by the change in GPS solution concentration over each 24-h time period.

To determine GPS sorption in both soils in the absence of PO_4, the above study was repeated identically, except without the addition of 50-mg L^{-1} PO_4 in the background solution. Statistical comparisons between fitted isotherm parameters were performed with the Tukey pairwise comparison procedure ($\alpha = 0.05$).

Glyphosate Transport in the Presence of Phosphate

Competitive sorption interactions between PO_4 and GPS within the soil environment under flow conditions were investigated. Miscible displacement transport experiments were performed in soil columns involving concurrent and consecutive pulses of GPS and PO_4. The concurrent pulse study was conducted to simulate a field situation where GPS and P fertilizer are applied very close in time, whereas the consecutive pulse studies are representative of a field situation where there is differential timing of herbicide and fertilizer applications. Acrylic columns (5-cm length, 6.4-cm i.d.) were uniformly packed with air dried homogenized soil. Columns were then slowly saturated with 5 mM KCl by upward flow supplied by a variable-speed-piston displacement pump. As the monovalent cation K^+ promoted dispersion of the Sharkey clay, which greatly restricted flow through the column, 5 mM $CaCl_2$ background solution was used for experiments involving this soil. Concurrent pulse experiments consisted of a mixed solution of 50-mg L^{-1} GPS and PO_4 (KH_2PO_4 at 71.65 mg L^{-1}) in background solutions of either 5 mM KCl (Commerce) or $CaCl_2$ (Sharkey). Consecutive pulse experiments involved single ion solutions of either 50-mg L^{-1} GPS or PO_4 in 5 mM KCl (Commerce) or $CaCl_2$ (Sharkey). The concurrent pulse was applied as a ~10-pore-volume pulse of the mixed ion solution applied to the column followed by leaching with 15 to 20 pore volumes of the background solution. Effluent was collected with an ISCO Retriever II fraction collector (Teledyne Isco). Concentrations of GPS in the effluent solution were determined by LSC and PO_4 concentrations were quantified by inductively coupled plasma atomic emission spectroscopy (ICP–AES, Spectro Citros CCD, SPECTRO Analytical Instruments). As GPS contains P, LSC-determined GPS concentrations were subtracted from ICP–AES values, and it was assumed that the difference would be P as PO_4^{3-}. Upon termination of the experiments, columns were then sectioned and residual radiolabeled compounds were extracted following a modified version of the method put forth by Miles and Moye (1988). Three grams of dried soil was weighed into 40-mL Teflon tubes, whereupon 30 mL of 0.2 M KOH was added. Tubes were then shaken for 24 h, and supernatant solutions were sampled and analyzed via LSC as described above. To determine sorbed-phase GPS degradation, extracting solutions were analyzed via ultra-performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS, Waters) to quantify the concentration of GPS and its primary metabolite, aminomethylphosphonic acid (AMPA).

For the consecutive pulse studies, the effect of the sequence of solute application (GPS then PO_4, and PO_4 then GPS) was investigated. Ten pore volumes of single-ion solutions were applied to columns and were subsequently leached with 15 to 20 pore volumes of background solution. After this initial leaching step, 10 pore volumes of single-ion solutions of the opposing solute were then applied and leached with 15 to 20 pore volumes of background solution. At the termination of experiments, columns were sectioned and residual radiolabeled compounds were extracted. Extracting solutions were then analyzed via LSC and UPLC–MS/MS.

To ensure quality of packing as well as to obtain independent estimates of the hydrodynamic dispersion coefficient *D*, a one pore volume pulse of tritium (^3H_2O) was applied to each column prior to the application of GPS or PO_4 and subsequently leached with background solution. Concentrations of tritium in the effluent solution were determined by LSC in a manner identical to that of GPS. Tracer breakthrough curves were described using the CXTFIT model (Toride et al., 1999) in the inverse mode to obtain estimates of the dispersion coefficient. Relevant physical parameters for each column transport study are given in Supplemental Table S2.

Results and Discussion

Soils

Pertinent physiochemical properties of both soils are given in Supplemental Table S1. The Commerce silt loam is characterized by a nearly neutral pH of 6.98, whereas the Sharkey clay is slightly more acidic with a pH of 6.52. Both soils have similar contents of total organic C, with Commerce and Sharkey containing 1.31 and 1.41%, respectively. The Sharkey soil has a cation exchange capacity of 29.6 cmol kg^{-1}, compared with a cation exchange capacity of 16.5 cmol kg^{-1} in the Commerce soil. The Commerce soil has a content of amorphous Fe and Al oxides of 4.4 and 0.7 g kg^{-1}, respectively, as determined by extraction with ammonium oxalate. These values were obtained from Harrell and Wang (2006), who conducted an earlier study involving Commerce soil collected from the same area. Sharkey has 0.83 and 0.23 g kg^{-1} of amorphous Fe and Al oxides, respectively. The content of Fe oxides determined by extraction with citrate bicarbonate dithionate is 6.08 g kg^{-1} in the Commerce soil and 7.77 g kg^{-1} in the Sharkey soil. Antecedent levels of soil P as quantified by the Mehlich-3 extraction procedure are 57.11 and 64.75 mg kg^{-1} in the Commerce and Sharkey soils, respectively.

Sorption and Desorption

Time-dependent Freundlich isotherms for GPS sorption by Commerce and Sharkey soils in the presence and absence of PO_4 are displayed in Fig. 1. The Freundlich isotherm is commonly used to describe equilibrium partitioning of a solute into solution and sorbed phases and is expressed as

$$S = K_f C^n \qquad [1]$$

where *S* is the sorbed concentration (mg kg^{-1}), K_f is the Freundlich partitioning coefficient (L kg^{-1}), *C* is the solution

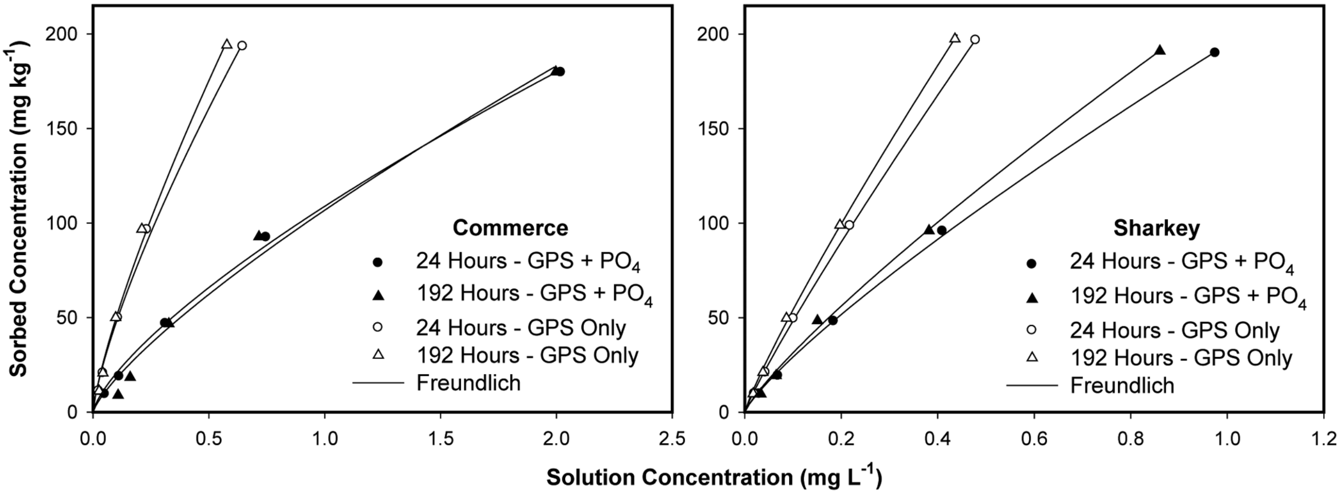

Fig. 1. Freundlich isotherms for glyphosate (GPS) sorption by Commerce and Sharkey soils with and without 50-mg L^{-1} PO$_4$ at 24 and 192 h of reaction time.

concentration (mg L^{-1}) and *n* is a dimensionless nonlinearity parameter commonly less than one. Corresponding values of the optimized Freundlich parameters are given in Table 1. Isotherm data were well described by the Freundlich model ($r^2 > 0.99$ in all cases), and GPS sorption by both soils was considerably reduced in the presence of PO$_4$. The 24-h Freundlich partitioning coefficients K_f were decreased from 272 to 109 L kg^{-1} and from 382 to 195 L kg^{-1} in the Commerce and Sharkey soils, respectively, when PO$_4$ was included in the background solution. This suggests significant competition between GPS and PO$_4$ ions for reactive sites in both matrices, with PO$_4$ being preferentially sorbed. These results are consistent with studies investigating competitive sorption between GPS and PO$_4$ by soils (de Jonge et al., 2001; Munira et al., 2016, 2018). Although GPS sorption decreased in the presence of PO$_4$, both soils exhibited relatively high affinities for solvated GPS. Gimsing et al. (2004a) attribute this to the presence of both competitive and ion-specific retention mechanisms, where herbicide association with competitive sites is decreased, but binding by GPS-specific sites was assumed to be unaffected. The relative reductions in Freundlich partitioning coefficients suggest that competition is somewhat more significant in the Commerce soil (∼60% reduction in K_f for Commerce vs. ∼50% reduction in K_f for Sharkey), likely due to the greater abundance of amorphous Fe and Al oxides, which are materials considered to have a high affinity for both GPS and PO$_4$ (Sprankle et al., 1975).

In the Freundlich isotherm model (Eq. [1]), the parameter *n* is a measure of the heterogeneity of the distribution of reactive site affinities across the range of input solution concentrations, with values closer to unity indicating a more homogenous system. In this case, the parameter *n* remained relatively consistent with time for both soils regardless of the absence or presence of PO$_4$. In fact, all optimized values of the Freundlich *n* for GPS sorption by the Commerce soil are not significantly different (Table 1). The same is also true for the Sharkey soil (Table 1). Similar findings exist for other solutes of interest. While investigating atrazine retention by sugarcane mulch residues and Commerce soil, Selim and Zhu (2005) reported that Freundlich *n* values remained constant between 2 and 504 h of reaction time. Additionally, Zhao and Selim (2010) found that the Freundlich *n* for describing Zn sorption by three different soils was independent of concentrations of P in solution. Directly comparable with our results, de Jonge et al. (2001) also reported reasonably consistent values of the Freundlich *n* for GPS sorption by soils with differential antecedent concentrations of P. The implications of this finding are significant, especially in regards to modeling applications. Models incorporating nonlinear sorption have previously been used to describe the time dependency

Table 1. Fitted Freundlich parameters for glyphosate (GPS) sorption in the presence and absence of PO$_4$ for Commerce and Sharkey soils.

Soil	Reaction time	Ions in solution	K_f ± 95% CI†	*n* ± 95% CI‡	SSE§	r^2
	h		L kg^{-1}		mg^2 kg^{-2}	
Commerce	24	GPS + PO$_4$	108.85 ± 7.35a¶	0.72 ± 0.09c	42.80	0.9978
	192	GPS + PO$_4$	106.79 ± 18.37a	0.78 ± 0.23c	274.59	0.9859
	24	GPS only	271.97 ± 33.84b	0.76 ± 0.13c	93.53	0.9958
	192	GPS only	300.67 ± 47.58b	0.78 ± 0.15c	127.26	0.9943
Sharkey	24	GPS + PO$_4$	194.65 ± 6.75a	0.82 ± 0.06c	12.97	0.9994
	192	GPS + PO$_4$	216.94 ± 13.04a	0.84 ± 0.09c	32.08	0.9985
	24	GPS only	382.32 ± 18.96b	0.90 ± 0.05c	7.61	0.9997
	192	GPS only	410.87 ± 27.43b	0.88 ± 0.06c	12.33	0.9995

† K_f, Freundlich partitioning coefficient; CI, confidence interval.

‡ *n*, dimensionless nonlinearity parameter.

§ SSE, sum of squared errors.

¶ Parameters followed by the same letters are not statistically different at α = 0.05. Parameters were not compared between soils.

of chemical retention by soils. These models, such as those put forth by Chen et al. (1996) and Selim and Amacher (1997), assume a time independency of the nonlinearity parameter. The observation of relatively constant Freundlich *n* values from this and previously mentioned studies lends credence to the applicability and suitability of such modeling approaches.

Fitted Freundlich isotherm parameters for GPS desorption from both soils are given in Supplemental Table S3. Desorption of GPS from both soils was enhanced by the presence of PO_4. Over two desorption steps, 12 to 19% of soil-bound GPS was desorbed from the Commerce soil in the presence of PO_4, compared with only 4 to 8% in the absence of PO_4. Similar results were obtained from the Sharkey soil where 7 to 9% of sorbed GPS was desorbed in the presence of PO_4, whereas only 3 to 5% was recovered when PO_4 was not included in the reacting solution. During desorption, the supernatant solution was replaced with a background solution that contains no GPS (5 mM KCl and 50-mg L^{-1} PO_4). This resulted in increased loading of PO_4 into the system, which subsequently displaced a greater amount of previously sorbed GPS. These findings are significant, as they demonstrate that not only is GPS sorption decreased in the presence of PO_4, but that additional PO_4 loading can mobilize the herbicide in the soil environment. Other studies have also determined that there is a propensity for PO_4 to displace soil-bound GPS from pure oxide minerals (Gimsing et al., 2004b), as well as from soils (Gimsing et al., 2004a; Gimsing et al., 2007; Simonsen et al., 2008).

Glyphosate Transport in the Presence of Phosphate: Consecutive Pulse Applications

The presence of the monovalent cation K^+ in solution caused dispersion of the Sharkey clay soil to the extent that flow in the soil columns was greatly restricted, so a background solution of $CaCl_2$ was used for transport experiments involving this soil. Inductively coupled plasma analysis of the input solutions indicated that PO_4 concentrations were almost negligible, most likely due to the precipitation of the anion as solid $Ca_3(PO_4)_2$. Gimsing and Borggaard (2001) also reported precipitation of PO_4 at similar concentrations in the presence of $CaCl_2$ while investigating sorption of GPS and PO_4 by goethite. Therefore, results and discussion of transport experiments will be limited to those involving only the Commerce soil.

The study in which GPS and PO_4 were applied as a mixed pulse will hereafter be referred to as the GPS+P column. Additionally, the consecutive pulse study where GPS is applied prior to PO_4 will be referred to as the GPS→P column, and the study in which PO_4 is applied prior to GPS will be referred to as the P→GPS column. The GPS and PO_4 breakthrough curves (BTCs) from the GPS→P column are displayed in Fig. 2. The figure on the left is meant to provide a clear illustration of GPS breakthrough in relation to the initial PO_4 BTC. Data in the figure on the right have a scale up to 8000 μg L^{-1} and better illustrate increased PO_4 concentrations in the effluent in the advanced stages of leaching. These results indicate that GPS mobility in the Commerce soil is highly limited, with only 2.1% of the applied mass recovered in the effluent solution and a peak concentration of 1.9% that of the input solution. The PO_4 pulse was applied at 27.6 pore volumes, as indicated by the vertical line in Fig. 2. After this application, a separate GPS BTC was observed and an additional 4% of the applied GPS mass was recovered in the effluent solution. This is an indication that the PO_4 pulse solution displaced existing soil-bound GPS. This can be explained by the presence of competitive and ion-specific reactive sites as described by Gimsing et al. (2004a). The GPS retained as a result of the applied GPS pulse is most likely associated with both competitive and ion-specific sites. Here, we assume that once a PO_4 pulse was introduced to the column, GPS bound to competitive sites was displaced and becomes mobile in the soil. This creates a kind of "cascading effect," where a secondary breakthrough is observed. Although the total mass recovered in the secondary breakthrough is relatively small compared with the mass applied, it is double that of the first BTC resulting from the GPS pulse. Furthermore, peak effluent concentrations in the secondary BTC are 44% greater than those of the first BTC. Therefore, PO_4 applications have a significant impact on the mobility of GPS in the Commerce soil. The PO_4–mediated displacement of GPS has been demonstrated in batch-type studies (Gimsing and Borggaard, 2001; Gimsing et al., 2004a, Simonsen et al., 2008); however, this is the first example of such an observation from laboratory column experiments to the best of our knowledge. These results are of significance, as inorganic P fertilizer applications after herbicide applications have the potential to mobilize GPS in this soil.

Phosphate mobility in the Commerce soil was somewhat limited, as indicated by the BTC displayed in the figure on the left. Considering only PO_4 breakthrough up to 59 pore volumes, 4.3% of the applied mass was recovered in the effluent solution and peak concentrations were 2.5% those of the input solution. After some 60 pore volumes, a secondary PO_4 breakthrough is observed, with effluent concentrations much greater than those measured in the initial breakthrough. Unfortunately, the experiment was terminated when appreciable radioactivity ceased to be measured in the effluent. Thus, unfortunately, PO_4 breakthrough data are unavailable beyond what are reported here. This secondary increase in PO_4 was not observed from the P→GPS column shown in Fig. 3 and is not correlated with any other changes in measurable parameters such as effluent pH, so it is unclear as to why this occurred. Further investigations to explain this observation are needed.

The GPS and PO_4 BTCs from the P→GPS column are presented in Fig. 3. Of the applied mass of PO_4, 4.5% was recovered in the effluent solution and peak concentrations were 3.4% that of the input solution. A lack of a secondary breakthrough of PO_4 on the application of GPS is an indication that GPS does not displace soil-bound PO_4, and thus PO_4 is preferentially sorbed in this soil, consistent with batch results. Glyphosate recovery in the effluent solution was 3.2% of the applied mass, and peak effluent concentrations were 2.7% of the input solution concentration. Here, GPS mobility was highly limited and there was no noticeable effect of competition between GPS and PO_4. This is in contrast with results reported by Zhao et al. (2009), where GPS mobility was decreased in a column preconditioned with PO_4. In their study, a saturated column was allowed to drain, whereupon PO_4 as KH_2PO_4 was dissolved in the collected leachate, and the subsequent solution was pumped back into the column and allowed to equilibrate overnight. This process likely induced a decrease in the system pH, especially near the inlet, which resulted in enhanced GPS sorption. Because the methods used in the Zhao et al. (2009) study are considerably different than those used here, a direct comparison

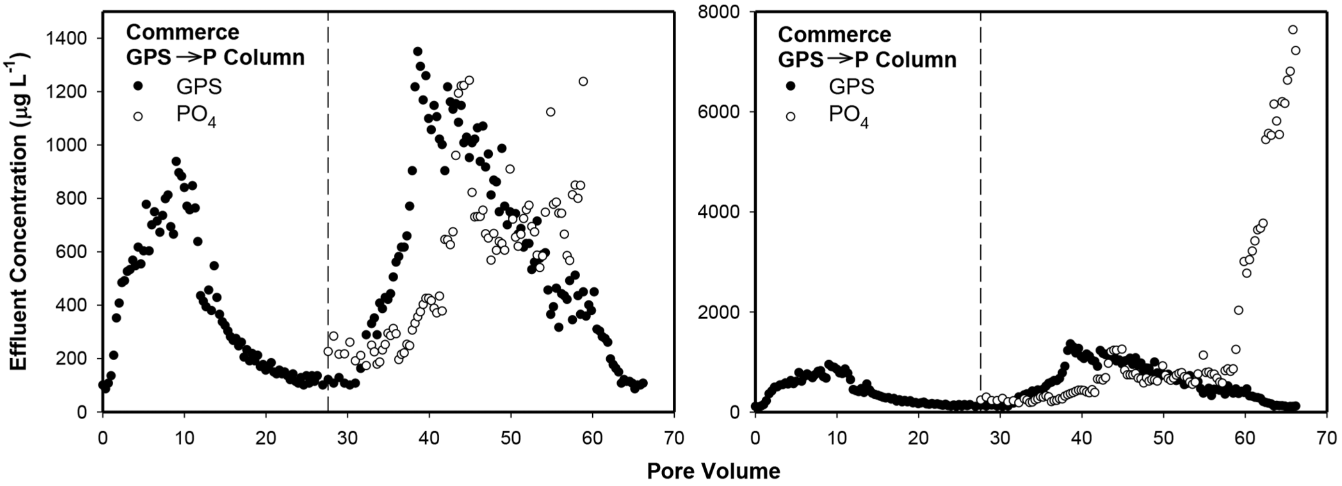

Fig. 2. Glyphosate (GPS) and PO$_4$ breakthrough from the Commerce GPS→P column. The dashed vertical line indicates when the PO$_4$ solution was applied.

between these two studies may not necessarily be valid. In terms of applicability to field conditions, applying GPS-based formulations onto soils with antecedent levels of inorganic P does not seem to enhance the mobility of the herbicide within the Commerce soil. Munira et al. (2016) as well as de Jonge and de Jonge (1999) demonstrated that GPS sorption by soils decreased when there were antecedent levels of PO$_4$ and concluded that the mobility of the herbicide may be increased in soils that have received historical applications of P fertilizers. However, these previous studies were conducted in a batch setting, and no further transport investigations were performed. The results of this study demonstrate that although batch results may indicate enhanced mobility by the presence of PO$_4$, further work is required to assess GPS mobility in a setting more similar to what would be expected under field and natural environmental conditions.

Glyphosate Transport in the Presence of Phosphate: Concurrent Pulse Applications

The GPS and PO$_4$ BTCs from the GPS+P column are displayed in Fig. 4. Surprisingly, the mobility of GPS remained highly limited in this soil column, with only 2.0% of the applied mass recovered in the effluent solution, and peak concentrations of just 1.8% those of the input concentration. This result was unexpected, as batch and GPS→P column results indicated significant competition between the two solutes for reactive sites, and thus enhanced GPS leaching was anticipated. There is an apparent lack of a PO$_4$ BTC as indicated by the P concentrations in the effluent solution determined by ICP analysis. This is in contrast with the GPS→P and P→GPS studies where a noticeable breakthrough was observed. The pH of the mixed ion input solution was 3.28 versus a pH of 5.09 for the PO$_4$–only solution. This decreased solution pH likely resulted in enhanced removal of PO$_4$ from the soil solution. A similar finding was reported by Barrow (1984), where the sorption of PO$_4$ by soils was increased at both low and high pH values of the reacting solution in five of six soils included in the study. Limited competition between GPS and PO$_4$ in transport settings was also observed by Barrett and McBride (2007), who demonstrated that herbicide applications did not mobilize antecedent PO$_4$. These results coupled with the results of the previous column studies imply that the timing of GPS-based herbicides and inorganic P fertilizer applications have major implications on the fate of GPS in the Commerce soil. Little effect was observed when both were applied in conjunction or when GPS was applied after a PO$_4$ pulse; however, enhanced GPS mobility may be expected when inorganic P is applied after herbicide applications.

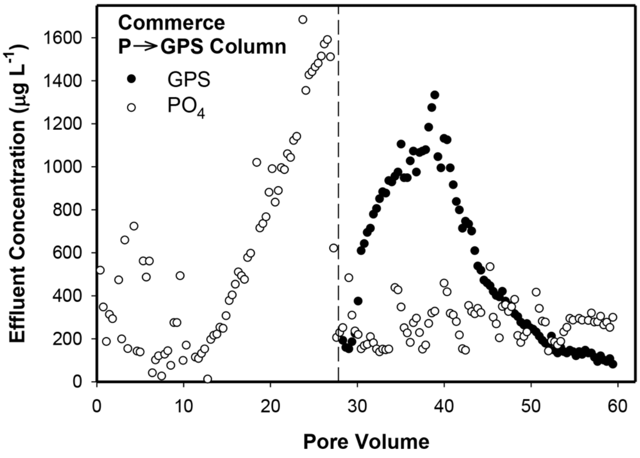

Fig. 3. Glyphosate (GPS) breakthrough from Commerce P→GPS column. The dashed vertical line indicates when the GPS solution was applied.

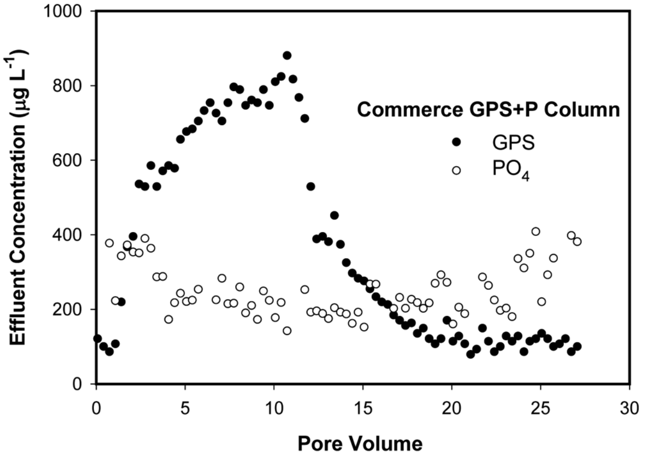

Fig. 4. Glyphosate (GPS) and PO$_4$ breakthrough from the Commerce GPS column.

Distribution of Residual Herbicide

Although it is difficult to assess the effect of competition between GPS and PO_4 in transport settings when only considering BTCs, a better understanding is gained when comparing the distribution of residual herbicide in the soil columns. The distributions of extracted radiolabeled compounds from each column experiment are displayed in Fig. 5, with calculated centers of mass (COM) given in Supplemental Table S5. Consistent with expectations for a strongly sorbing solute, residual mass is concentrated near the inlet port and decreases rapidly with depth. The herbicide distribution from the GPS→P column is consistent with GPS concentrations observed in the effluent. Here, there is some depletion of GPS near the inlet port and subsequent enrichment of herbicide concentrations further into the column. This provides added evidence that PO_4 in solution displaced GPS bound on competitive sites and essentially "pushed" the mass of GPS to lower depths in the soils column until a secondary breakthrough was observed. This is further emphasized by the calculated COM (1.40 cm from the inlet), which is the deepest of all three transport experiments. A comparison between the GPS+P column distribution and that obtained from the P→GPS column provides additional insight into the effects of competition. The relatively large amount of GPS in the first 1 cm of the P→GPS column suggests that bound PO_4 does not limit the availability of reactive sites. The lower GPS mass extracted from the first 1 cm of the GPS+P column relative to the P→GPS column suggests that the major consequence of the concurrent application of GPS and PO_4 is that the kinetics of GPS sorption is prolonged by the coexistence of solvated PO_4. Since GPS sorption is not limited by site availability, competition between the two solutes for competitive sites may keep GPS in the liquid phase for a longer period of time, such that mass advection plays a more dominant role and subsequently transports GPS in solution further into the column. As retention rapidly reduces solution concentration while the number of reactive sites remains high, this effect is only apparent in the soil closest to the inlet port.

A lack of prolonged radioactivity measured in the effluent solution suggests that the ^{14}C remains associated with the phosphonomethyl group, indicating that degradation of GPS is via the AMPA pathway. If it is assumed that any degradation beyond AMPA will result in a readily mineralized compound, fractions of GPS and AMPA determined with UPLC–MS/MS can be applied to extract concentrations obtained via LSC to obtain distributions of both compounds in each transport experiment. Distributions are displayed in Supplemental Fig. S1 with calculated COM for either compound given in Supplemental Table S5. Assuming that rates of degradation are constant in each section of the soil column despite the differential sorbed phase concentrations, AMPA is more mobile than GPS in all cases, with calculated COM deeper in the soil column. This may be attributable to degradation of solution phase or easily exchangeable GPS, which are herbicide pools more liable to degradation (Eberbach, 1998). The AMPA generated from these pools would likely be more mobile in the soil, resulting in a lower COM for the bulk AMPA distribution. These findings are consistent with results from a separate study (results not given), which suggest a lower affinity of the Commerce soil for AMPA. Despite a lower distribution of AMPA in the soil column relative to GPS, both solutes are strongly retained.

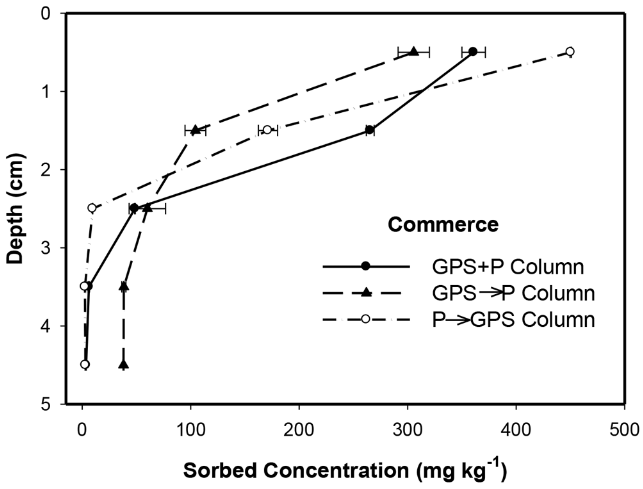

Fig. 5. Distribution of radiolabeled compounds extracted from each column. Error bars are 95% confidence intervals. GPS, glyphosate.

Conclusions

Results of batch experiments indicate significant competition between GPS and PO_4 in both soils, with 60 and 50% reductions in the 24-h Freundlich partitioning coefficients for the Commerce and Sharkey soils, respectively. Increased loading of PO_4 during desorption resulted in enhanced release of soil-bound GPS from both soils. This indicates a propensity for PO_4 to displace GPS from reactive sites. Although K_f was decreased, both soils exhibited a high affinity for GPS even in the presence of PO_4. This suggests the presence of a significant amount of both competitive and ion-specific sites. Results of transport studies suggest that the mobility of GPS in the Commerce soil is highly limited when applied in conjunction with or after the application of inorganic P. However, application of a PO_4 pulse after GPS application did result in a secondary BTC, from which an additional 4% of applied GPS was recovered. This result is further emphasized by the distribution of soil-bound residues extracted from this column, with a depletion of mass near the inlet and enrichment of mass at lower depths, indicating that PO_4 displaced the bulk mass of GPS further into the column. Analyses of the distribution of residuals from the GPS column and P→GPS columns suggest that the main effect of the coapplication of the solutes is that GPS retention kinetics are prolonged, which allows for enhanced mobility brought about by mass advection processes. These results emphasize the importance of herbicide and fertilizer application timing under field conditions. Specifically, these findings demonstrate that soil-bound GPS may be more liable to mobilization and subsequent leaching in scenarios in which inorganic P is applied after herbicide applications. This may be especially relevant in situations in which weed management or chemical fallow occur prior to soil amendment via fertilizer application.

Supplemental Material

The supplemental material available online includes four tables and one figure.

References

Barrett, K.A., and M.B. McBride. 2007. Phosphate and glyphosate mobility in soil columns amended with Roundup. Soil Sci. 172:17–26. doi:10.1097/01.ss.0000240549.44551.3d

Barrow, N.J. 1984. Modelling the effects of pH on phosphate sorption by soils. J. Soil Sci. 35:283–297. doi:10.1111/j.1365-2389.1984.tb00283.x

Benbrook, C. 2016. Trends in glyphosate herbicide use in the United States and globally. Environ. Sci. Eur. 28:3. doi:10.1186/s12302-016-0070-0

Bott, S., T. Tesfamariam, A. Kania, B. Eman, N. Aslan, V. Römheld, and G. Neumann. 2011. Phytotoxicity of glyphosate soil residues re-mobilised by phosphate fertilisation. Plant Soil 342:249–263. doi:10.1007/s11104-010-0689-3

Chen, J.S., R.S. Mansell, P. Nkedi-Kizza, and B.A. Burgoa. 1996. Phosphorus transport during transient, unsaturated water flow in an acid soil. Soil Sci. Soc. Am. J. 60:42–48. doi:10.2136/sssaj1996.03615995006000010009x

Cornish, P.S. 1992. Glyphosate residues in a sandy soil affect tomato transplants. Aust. J. Exp. Agric. 32:395–399. doi:10.1071/EA9920395

de Jonge, H., and L.W. de Jonge. 1999. Influence of pH and solution composition on the sorption of glyphosate and prochloraz to a sandy loam soil. Chemosphere 39:753–763. doi:10.1016/S0045-6535(99)00011-9

de Jonge, H., L.W. de Jonge, O.H. Jacobsen, T. Yamaguchi, and P. Moldrup. 2001. Glyphosate sorption in soils of different pH and phosphorus content. Soil Sci. 166:230–238. doi:10.1097/00010694-200104000-00002

Dideriksen, K., and S.L.S. Stipp. 2003. The adsorption of glyphosate and phosphate to geothite: A molecular-scale atomic force microscopy study. Geochim. Cosmochim. Acta 67:3313–3327. doi:10.1016/S0016-7037(02)01369-8

Eberbach, P. 1998. Applying non-steady-state compartmental analysis to investigate the simultaneous degradation of soluble and sorbed glyphosate (*N*-(phophonomethyl)glycine) in four soils. Pest Manag. Sci. 52:229–240. doi:10.1002/(SICI)1096-9063(199803)52:3<229::AID-PS684>3.0.CO;2-O

Geelhoed, J.S., T. Hiemstra, and W.H. Reimsdijk. 1998. Competitive Interaction between phosphate and citrate on goethite. Environ. Sci. Technol. 32:2119–2123. doi:10.1021/es970908y

Gimsing, A.L., and O.K. Borggaard. 2001. Effect of KCl and $CaCl_2$ as background electrolytes on the competitive adsorption of glyphosate and phosphate on goethite. Clays Clay Miner. 49:270–275. doi:10.1346/CCMN.2001.0490310

Gimsing, A.L., O.K. Borggaard, and M. Bang. 2004a. Influence of soil composition on adsorption of glyphosate and phosphate by contrasting Danish surface soils. Eur. J. Soil Sci. 55:183–191. doi:10.1046/j.1365-2389.2003.00585.x

Gimsing, A.L., O.K. Borggaard, and P. Sestoft. 2004b. Modeling the kinetics of the competitive adsorption and desorption of glyphosate and phosphate on goethite and gibbsite and in soils. Environ. Sci. Technol. 38:1718–1722. doi:10.1021/es030572u

Gimsing, A.L., C. Szilas, and O.K. Borggaard. 2007. Sorption of glyphosate and phosphate by variable-charge tropical soils from Tanzania. Geoderma 138:127–132. doi:10.1016/j.geoderma.2006.11.001

Gomes, M.P., S.G. Le Manac'h, M. Moingt, E. Smedbol, S. Paquet, M. Labrecque, et al. 2016. Impact of phosphate on glyphosate uptake and toxicity in willow. J. Hazard. Mater. 304:269–279. doi:10.1016/j.jhazmat.2015.10.043

Gomes, M.P., S. Maccario, M. Lucotte, M. Labrecque, and P. Juneau. 2015. Consequences of phosphate application of glyphosate uptake by roots: Impacts for environmental management practices. Sci. Total Environ. 537:115–119. doi:10.1016/j.scitotenv.2015.07.054

Harrell, D.L., and J.J. Wang. 2006. Fractionation and sorption of inorganic phosphorus in Louisiana calcareous soils. Soil Sci. 171:39–51. doi:10.1097/01.ss.0000187347.37825.46

Kanissery, R.G., A. Welsh, and G.K. Sims. 2015. Effect of soil aeration and phosphate addition on the microbial bioavailability of carbon-14-glyphosate. J. Environ. Qual. 44:137–144. doi:10.2134/jeq2014.08.0331

Kruse, J., M. Abraham, W. Amelung, C. Baum, R. Bol, O. Kühn, et al. 2015. Innovative methods in soil phosphorus research: A review. J. Plant Nutr. Soil Sci. 178:43–88. doi:10.1002/jpln.201400327

Lu, X., B. Zhou, J. Zhang, J. Deng, and X. Sun. 2005. Influence of phosphate on the mobility of pesticide glyphosate in different soils. China Environ. Sci. 25:607–610.

Miles, M., and H.A. Moye. 1988. Extraction of glyphosate herbicide from soil and clay minerals and determination of residues in soils. J. Agric. Food Chem. 36:486–491. doi:10.1021/jf00081a020

Munira, S., A. Farenhorst, and W. Akinremi. 2018. Phosphate and glyphosate sorption in soils following long-term phosphate applications. Geoderma 313:146–153. doi:10.1016/j.geoderma.2017.10.030

Munira, S., A. Farenhorst, D. Flaten, and C. Grant. 2016. Phosphate fertilizer impacts on glyphosate sorption by soil. Chemosphere 153:471–477. doi:10.1016/j.chemosphere.2016.03.028

Okada, E., D. Pèrez, E.D. Gerónimo, V.C. Aparicio, H. Massone, and J.L. Costa. 2018. Non-point source pollution of glyphosate and AMPA in a rural basin from the southeast Pampas, Argentina. Environ. Sci. Pollut. Res. Int. 25:15120–15132. doi:10.1007/s11356-018-1734-7

Primost, J.E., D.J.G. Marino, V.C. Aparicio, J.L. Costa, and P. Carriquiriborde. 2017. Glyphosate and AMPA, "pseudo-persistent" pollutants under real-world agricultural management practices in the Mesopotamic Pampas agroecosystem, Argentina. Environ. Pollut. 229:771–779. doi:10.1016/j.envpol.2017.06.006

Selim, H.M. 2014. Transport and fate of chemicals in soils: Principles and applications. CRC Press, Boca Raton, FL. doi:10.1201/b17405

Selim, H.M., and M.C. Amacher. 1997. Reactivity and transport of heavy metals in soils. CRC Press, Boca Raton, FL.

Selim, H.M., and H. Zhu. 2005. Atrazine sorption-desorption hysteresis by sugarcane mulch residue. J. Environ. Qual. 34:325–335. doi:10.2134/jeq2005.0325

Simonsen, L., I.S. Fomsgaard, B. Svensmark, and N.H. Spliid. 2008. Fate and availability of glyphosate and AMPA in agricultural soil. J. Environ. Sci. Health Part B 43:365–375. doi:10.1080/03601230802062000

Sprankle, P., W.F. Meggit, and D. Penner. 1975. Adsorption, mobility, and microbial degradation of glyphosate in the soil. Weed Sci. 23:229–234.

Toride, N., F.J. Leij, and M.T. van Genuchten. 1999. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, Version 2.1. Res. Rep. 137. US Salinity Lab., USDA- ARS, Riverside, CA.

Zhao, B., J. Zhang, J. Gong, H. Zhang, and C. Zhang. 2009. Glyphosate mobility in soils by phosphate application: Laboratory column experiments. Geoderma 149:290–297. doi:10.1016/j.geoderma.2008.12.006

Zhao, K., and H.M. Selim. 2010. Adsorption-desorption kinetics of Zn in soils: Influence of phosphate. Soil Sci. 175:145–153. doi:10.1097/SS.0b013e3181dd51a0