Time-Dependent Sorption and Desorption of Glyphosate in Soils: Multi-reaction Modeling

Joshua T. Padilla and H. Magdi Selim*

The herbicide glyphosate \(\text{[N-(phosphonomethyl) glycine]}\) (GPS) is commonly found offsite of application areas, despite traditional presumptions of the compound's immobility in the environment. This suggests that further efforts to predict the behavior and fate of GPS in soils are needed. In this study, kinetic batch experiments were conducted to assess the time-dependent sorption and desorption of GPS by two agricultural soils from southern Louisiana: Commerce silt loam (a fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquept) and Sharkey clay (a very-fine, smectitic, thermic Chromic Epiaquert). Results of batch experiments indicate a high affinity of both soils for GPS, with 24-h Freundlich coefficients of 158 and 396 L\(^n\) mg\(^{-n}\) kg\(^{-1}\) for the Commerce and Sharkey soils, respectively. An apparent time dependency of GPS sorption by both soils was observed, especially within the first 72 h. Changes in solution concentrations of the herbicide beyond 72 h are attributed to both additional sorption as well as solution-phase degradation. A two-site multi-reaction model incorporating time-dependent reversible and irreversible reactions successfully described the measured data from the batch experiments. However, values of the rate coefficients and sorbed concentrations may be overestimated due to the model's inability to account for degradation processes. Analysis of extracted soil-bound residues illustrates that degradation of sorbed phase GPS is significant in both soils, although it occurs to a greater extent in the Sharkey soil. Degradation of the herbicide probably occurs through the aminomethylphosphonic acid pathway, as \(^{14}\text{C}\) remained associated with the phosphonomethyl group. Models that account for both time-dependent reactions and degradation will probably lead to improved predictions of the fate of GPS in soils.

Abbreviations: AMPA, aminomethylphosphonic acid; GPS, glyphosate; LSC, liquid scintillation counter; MRM, multi-reaction model; UPLC-MS/MS, ultra-performance liquid chromatography–tandem mass spectrometry.

Glyphosate is a broad-spectrum, nonselective, post-emergence herbicide used pervasively throughout the world. The introduction of GPS into the environment takes place mostly via herbicide application for commercial agricultural production, although urban use also represents significant environmental loading (Zgheib et al., 2012; Ramwell et al., 2014). Traditionally, GPS is considered to be relatively immobile in soils due to its high sorption capacity and rapid degradation (Borggaard and Gimsing, 2008). However, the occurrence of GPS and its main metabolite, aminomethylphosphonic acid (AMPA), in riparian groundwater in an agricultural basin in Canada (Van Stempvoort et al., 2014) as well as in surface waters in Argentina (Aparicio et al., 2013; Berman et al., 2018) lend credence to the notion that the herbicide’s mobility in soil is of environmental concern. Additionally, recent studies indicating the potential of cytotoxic (Richard et al., 2005; Koller et al., 2012) as well as carcinogenic effects (Myers et al., 2016) of GPS itself further emphasize the necessity to characterize the herbicide’s behavior and ultimate fate in the environment.

Studies aimed at quantifying the sorption and desorption of GPS in soils and minerals are numerous (Borggaard and Gimsing, 2008). The high retentive capacities of GPS in soil have been attributed mainly to the reactivity of the phosphonomethyl functional group of the GPS molecule (Sprankle et al., 1975; Glass, 1987; Borggaard and Gimsing, 2008; Gros et al.,
2017), although interactions with the carboxymethyl group have been shown to be significant in limited cases (Dideriksen and Stipp, 2003). Glyphosate sorption in soils has been positively correlated with the presence of amorphous Fe and Al oxides (Sprankle et al., 1975; Sheals et al., 2002; Gimsing et al., 2007), as well as with soil clay content and cation exchange capacity (Glass, 1987; Sidoli et al., 2016; Gros et al., 2017). Conversely, GPS sorption has been negatively correlated with pH (Glass, 1987; Gimsing and Borrgaard, 2007; Pessagno et al., 2008) due to its polyprotic behavior and propensity to deprotonate at higher pH values. The role of organic matter in GPS sorption is a relatively ambiguous subject, with some studies reporting increased GPS retention by organic matter (Yu and Zhou, 2005; Albers et al., 2009) while others have reported enhanced mobility of GPS due to increased soil organic matter concentrations (Gerritse et al., 1996; Arroyave et al., 2016). In general, GPS sorption onto mineral surfaces is considered a rapid process (Borrgaard and Gimsing, 2008; Ozbay et al., 2018) and therefore, efforts to describe the solution–solid phase partitioning have largely used equilibrium models. A major limitation to these descriptions is that they ignore time-dependent chemical processes, which have been documented with GPS–soil interactions. Gerritse et al. (1996) observed significant increases in the amount of GPS sorbed by Australian soils beyond 24 h of reaction time. Similar results were reported by Gimsing et al. (2004a), where increases in the sorbed concentrations of GPS by Danish soils occurred during a period of 7 d. Their results suggest that models that can account for the time dependency of GPS sorption by soils may provide more accurate predictions of the behavior and ultimate fate of the herbicide in the environment than those that consider only equilibrium partitioning. Gimsing et al. (2004c) well described batch study data of GPS and phosphate sorption by soils and pure minerals with the use of various kinetic models; however, only one input concentration was evaluated and only sorption was considered (desorption was not included). To our knowledge, no other studies have been focused on describing GPS batch sorption data with time.

The goals of this study were to: (i) evaluate the time-dependent sorption–desorption behavior of GPS in two Louisiana agricultural soils, and (ii) apply a multi-reaction model to describe observations obtained from kinetic batch studies.

Methods

Soils

Two commonly cultivated surface soils from Louisiana were used in this study; Commerce silt loam (30% sand, 54% silt, 16% clay, pH 6.98) and Sharkey clay (3% sand, 36% silt, 61% clay, pH 6.52). Both soils were sampled from surface horizons (0–5 cm) near Iberville Parish, LA, air dried, and made to pass through a 2-mm sieve prior to the experiments. Select physicochemical properties of both soils are provided in Supplemental Table S1.

Adsorption and Desorption

The quantification of sorption and desorption of GPS in the two different soils was performed following the batch technique described by Selim (2014). Three grams of soil was weighed into a 40-mL Teflon centrifuge tube, and 30 mL of GPS solution at an initial concentration of either 1, 2, 5, 10, or 20 mg L⁻¹ was added to each tube. Input solutions were spiked with ¹⁴C-labeled GPS (phosphonomethyl group) such that the initial radioactivity of each solution was approximately 1.67 × 10² Bq mL⁻¹. Radiolabeled GPS was purchased from American Radiolabeled Chemicals. All solutions were prepared in a 5 mM CaCl₂ background solution to maintain constant ionic strength. Each initial concentration treatment was repeated in triplicate. Soil–solution mixtures were then individually vortexed for 10 s, immediately transferred to a platform shaker, and continuously shaken at a temperature of 21 ± 1°C throughout the duration of the study. To determine sorption characteristics with time, samples were taken at 2, 4, 8, 12, 24, 72, 192, 360, and 528 h. This was done by centrifuging the tubes at 11,000 × g 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) were then added, and the mixtures were vortexed until thoroughly 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 compared with that of the input solution. To minimize the effect of degradation within the sampled aliquot, samples were either read the same day or frozen prior to analysis. For the highest input concentration (20 mg L⁻¹), 3 mL of solution was removed at the 72-h sampling time. Of this volume, a 1-mL aliquot was used for LSC analysis while the additional 2 mL was frozen for further analysis by ultra-performance liquid chromatography–tandem mass spectrometry (UPLC-MS/MS). This was performed to determine the extent of degradation of solution-phase GPS to AMPA during the first 72 h.

Desorption, based on successive dilutions, commenced immediately after the last sorption step. At the 528-h sampling, the remaining supernatant was decanted and replaced with 30 mL of the background solution (5 mM CaCl₂). The mixtures were then shaken for 72 h, centrifuged, and the supernatant was decanted and replaced with 30 mL of background solution. This process was repeated for a total of five desorption steps during a 15-d time period. One-milliliter aliquots at each sampling time were analyzed using LSC in the same manner as described above. At the last desorption step, the supernatant was decanted and the remaining soil pellets were refrigerated until extraction.

All individual tubes were weighed prior to and after sampling during the sorption experiments. Similarly, all tubes were weighed prior to and after the decanting of the supernatant, as well as after the addition of background solution during the desorption experiments. This was done so that there was an accounting of the mass of solution removed from, and within, the sample tubes at all times. In this way, the sorbed concentration of GPS at each time step was determined through simple mass balance calculations.
Extraction of residual GPS was performed following desorption (37 d after the initial application of GPS) using a modified version of the method described by Miles and Moyer (1988). Here, 30 mL of 0.2 M KOH was added to each tube, and the mixtures were vortexed and then shaken for 24 h with a platform shaker. The tubes were then centrifuged for 10 min at 11,000 × g, and supernatants were collected. One-milliliter aliquots of supernatant extracting solution were analyzed using LSC following the method described above.

Analysis of Extracted Residues

Because significant microbial degradation has been reported to occur during the time steps used in the batch experiments, efforts were made to quantify the amount of AMPA in the supernatant solutions and within the soil-bound residues. Because both GPS and AMPA molecules have the 14C-labeled phosphonomethyl group, LSC analysis alone cannot discriminate between the two compounds. To do this, selected samples were analyzed using UPLC-MS/MS with a pre-column derivatization and solid-phase extraction cleanup procedure. Specific details pertaining to this procedure are provided in the Supplemental Material. Samples that were analyzed via UPLC-MS/MS were supernatant solutions collected from the highest input concentrations at 72 and 528 h, along with the KOH extracting solutions from all input concentrations. For the extracting solutions, 1-mL aliquots collected from each triplicate were combined and thoroughly mixed to produce a composite sample for analysis by UPLC-MS/MS.

Mineralization of Glyphosate

Large discrepancies in mass balance on the termination of batch studies suggested that loss of applied radioactivity due to complete GPS mineralization to 14CO2 was significant in both soils. To confirm this, a degradation study meant to replicate batch conditions was performed. Degradation experiments involving both soils were completed in duplicate. Three grams of soil was weighed into a stirred reactor apparatus with a total volume of 50 mL. Thirty milliliters of 100 mg L−1 GPS in 5 mM CaCl2 was added to the soil, and the reactor was immediately sealed. Sealed reactors with soil–solution mixtures were then placed atop magnetic stir plates such that a homogenous soil suspension was maintained throughout the duration of the study. A 3.2-mm-thick extruded polystyrene foam insulating pad was placed between the reactor and stir plate to minimize heat transfer between the two. Two ports on top of the reactor lid allowed sampling of the headspace gases. One port (P1) was in direct contact with a 2-mL 1 M NaOH CO2 trap in a 10-mL borosilicate glass test tube via Tygon tubing fed into a 25-gauge needle. Test tubes were sealed with Parafilm to prevent evaporation of the NaOH solution as well as gas exchange with the ambient atmosphere. The second port (P2) was connected to a length of Tygon tubing that remained clamped except during sampling. During sampling, a 60-mL syringe was connected to P2 and was used to slowly flush the internal headspace with 60 mL of ambient atmosphere. This was repeated for a total flushing volume of 120 mL. After this, 1 mL of the NaOH trap solution was analyzed via LSC as described above. The NaOH traps were replaced after each sampling. A picture of the experimental setup during sampling is given in the Supplemental Material. The headspace gas inside the reactor was sampled at 24, 72, 192, 360, 528, 696, 864, and 1128 h (1–47 d). Because CO2 is the only volatile metabolite of GPS, any radioactivity measured in the NaOH trap solution was taken to be 14CO2 directly evolved from the degradation of the labeled herbicide.

Multi-reaction Model

Soils are inherently heterogeneous in their physiochemical composition, and as such, it is reasonable to expect that a solute will interact with different soil constituents at different rates. It then follows that a description of GPS sorption that considers differences in reaction rates is likely to have greater predictive capabilities than one that does not. One such model that considers various rates of sorption reactions is the multi-reaction model (MRM) put forth by Selim and Amacher (1997). Indeed, the MRM has been successful in describing the behavior of a wide range of reactive chemicals in soil (Selim, 2014). Assumptions of this model are that sorbed species are retained by various sites exhibiting different affinities and that chemical nonequilibrium conditions exist. Presented here is a specialized case of the MRM that considers two general types of reactions. The first type is a reversible reaction:

\[
\rho \frac{\partial S_1}{\partial t} = \theta k_1 C^n - \rho k_2 S_1 \quad [1]
\]

where \(\rho\) (g cm\(^{-3}\)) is the soil bulk density, \(\theta\) is the soil moisture content, \(k_1\) and \(k_2\) (h\(^{-1}\)) are forward and backward rate coefficients, respectively, \(C\) is the solution concentration (mg L\(^{-1}\)), \(S_1\) (mg kg\(^{-1}\)) is the sorbed concentration retained on reversible sites, and \(n\) is the reaction order. A feature of the use of the \(n\) parameter is that nonlinear sorption by soils, which is often observed, is accounted for by the MRM. The second type of reaction considered is an irreversible reaction:

\[
\rho \frac{\partial S_{irr}}{\partial t} = \theta k_{irr} C \quad [2]
\]

where \(k_{irr}\) (h\(^{-1}\)) is a rate coefficient for irreversible reactions, and \(S_{irr}\) (mg kg\(^{-1}\)) is the sorbed concentration retained on irreversible sites. The total sorbed concentration \((S_T)\) is given by

\[
S_T = S_1 + S_{irr} \quad [3]
\]

It is important to note that the above expressions do not imply specific retention mechanisms but rather only a difference in reaction rates for general types of sites (i.e., reversible or irreversible sites). As such, a detailed knowledge of the chemical makeup of the soils is not needed to apply the MRM. Data obtained from batch experiments were modeled with the MRM using the publically available Chem_Transport software (www.spess.lsu.edu/chem_transport/).
Statistical Analysis

The Freundlich isotherm parameters for the GPS sorption data at each sampling time were obtained using the PROC NLIN procedure in SAS 9.4 statistics software (SAS Institute). The goodness-of-fit of the Freundlich isotherm to the measured data was characterized by the sum of squared errors (SSE) and the \( r^2 \) value. A comparison between the fitted isotherm parameters was done using the Tukey pairwise comparison procedure (\( \alpha = 0.05 \)). The MRM parameters were optimized using the Levenberg–Marquardt nonlinear least squares optimization procedure (Press et al., 1992). The goodness-of-fit of the model is characterized by the \( r^2 \) value, as well as by the root mean squared error (RMSE):

\[
\text{RMSE} = \sqrt{\frac{\text{RSS}}{n_{\text{obs}} - n_{\text{par}}}}
\]

where RSS is the residual sum of squares, \( n_{\text{obs}} \) is the number of observations, and \( n_{\text{par}} \) is the number of fitted parameters.

Results and Discussion

Glyphosate Adsorption and Desorption

The time-dependent sorption isotherms of GPS in both soils are displayed in Fig. 1. The experimental data were well described by the Freundlich model (\( r^2 \geq 0.995 \) in all cases), with optimized parameter values given in Table 1. In general, Freundlich coefficients increased throughout the sorption experiments and ranged from 130.4 to 317.8 L\(^n\) mg\(^{1-n}\) kg\(^{-1}\) and 206.4 to 471.4 L\(^n\) mg\(^{1-n}\) kg\(^{-1}\) for the Commerce and Sharkey soils, respectively. These values indicate a high affinity of both matrices for GPS and are consistent with those obtained from similar studies performed on a variety of soils (Sidoli et al., 2016; Gros et al., 2017; Zhelezova et al., 2017). The values of the Freundlich \( K_f \) coefficient, along with the lower solution-phase concentrations of GPS at the various sampling times, indicate that the Sharkey soil exhibits a higher affinity than the Commerce soil. The high affinity of the Commerce soil may be attributed to the relatively high content of amorphous Fe and Al oxides, which are materials with a demonstrated high affinity for GPS (Sprankle et al., 1975; Sheals et
al., 2002; Gimsing et al., 2007). The high cation exchange capacity of the Sharkey soil probably allows GPS complex formation with surface exchangeable polyvalent cations (probably Ca$^{2+}$ in this case) (de Jonge and de Jonge, 1999; Dollinger et al., 2015), although ligand exchange at edge sites of layer silicates may also be of significance (Borggaard and Gimsing, 2008).

The 2-h sorption isotherm for the Sharkey soil, as well as the 2- to 24-h isotherms for the Commerce soil, are characterized as highly nonlinear ($n < 0.70$). This indicates that the rate of partitioning of GPS between solution and sorbed phases (slope of the isotherm) is dependent on the solution concentration at these sampling times. The value of $n$ increased modestly during the sorption experiments (isotherms became more linear), which has been observed for other organic compounds (Ma et al., 1993; Selim and Zhu, 2005). Changes in fitted isotherm parameters with time is also an indication of sorption kinetics, with significant differences in the Freundlich $K_f$ value occurring up to 192 and 72 h for the Commerce and Sharkey soils, respectively. While kinetics were observed with both soils, the time dependence of sorption was less pronounced in the Sharkey soil, as indicated by the small changes in solution concentrations of GPS between sampling times relative to the Commerce soil. Although several studies have indicated that GPS sorption onto soils reaches pseudo-equilibrium conditions in 2-24 h or less (Piccolo et al., 1994; Borggaard and Gimsing, 2008; Keshteli et al., 2011), significant kinetics following a 24-h equilibration time were also reported by Gerritse et al. (1996) using sandy soils from Western Australia. Additionally, Gimsing et al. (2004a) observed significant increases in GPS adsorption during 50 h, with limited increases continuing up to 168 h in selected Danish surface soils, a result that was again observed with variously charged soils from Tanzania (Gimsing et al., 2007). Relative changes in the solution concentrations of GPS at each sampling time increased with increasing input concentrations, especially within the early time steps (2–72 h). This suggests that the extent of kinetics depends on the amount of GPS within the system, with low GPS inputs equilibrating with soils on shorter time scales than higher GPS inputs.

Because microbial degradation of GPS in solution is generally considered a rapid process (Simonsen et al., 2008; Al-Rajab and Schiavon, 2010; Yang et al., 2015), the perceived kinetics of GPS adsorption by soils may be attributed to biotic mineralization in the solution phase, i.e., reductions in solution-phase GPS may be due to degradation rather than additional sorption. However, UPLC-MS/MS analyses indicated that approximately 92 and 80% of the measured radioactivity in the supernatant solutions at 72 h can be attributed to GPS for the Sharkey and Commerce soils, respectively. This would suggest that the majority of the change in solution concentration of GPS between 2 and 72 h is due to additional sorption onto the soils rather than microbial degradation. It is unclear as to the magnitude of the effect of microbial degradation beyond 72 h because supernatant concentrations of GPS and AMPA were not monitored with time, although AMPA in the supernatant solution at 528 h accounted for only 16% of the measured radioactivity for the Commerce soil. Due to these findings, microbial degradation accounted for only limited changes in solution concentrations of GPS in the Commerce batch study, and therefore increased sorption with time can be mainly attributed to kinetics. Important to note is the fact that Freundlich isotherm parameters were not adjusted for the presence of AMPA in solution. This is because a proper adjustment of the isotherms would also need to account for the sorbed-phase composition (i.e., sorbed concentrations of GPS and AMPA), which cannot be obtained without destructive sampling. Therefore, the Freundlich coefficients refer to solution- and sorbed-phase concentrations of GPS and AMPA as a whole and do not discriminate between the two compounds.

For the Sharkey soil, there is a more apparent effect of herbicide degradation. Although AMPA accounted for only minimal amounts of solution radioactivity at 72 h, UPLC-MS/MS analysis indicated that approximately 66% of the measured radioactivity at 528 h was attributed to the metabolite. Because of this, it is likely that the observed retention kinetics beyond 72 h were largely due to microbial degradation of solution-phase GPS. However, it is expected that the implications of greater degradation of solution-phase GPS in the Sharkey batch study are minimal because changes in the solution-phase concentrations beyond 72 h are limited (Fig. 1) and Freundlich coefficients obtained at 72 h and beyond are not significantly different at $a = 0.05$ (Table 1).

Desorption of GPS from both Commerce and Sharkey soils was highly limited, indicating strong sorption–desorption hysteresis in both soils. Desorption isotherms are displayed in Fig. 2. During five desorption steps in 15 d, only 2.3 to 3.4% of the sorbed mass was recovered in the desorption supernatant solutions for the Commerce soil. A similar trend was observed for the Sharkey soil, with only 1.9 to 2.5% of the sorbed mass recovered in the desorbing solutions. This would suggest that sorbed-phase GPS in both soils is associated mainly with irreversible reactive sites. Low recovery during desorption can also be attributed to full mineralization of the herbicide, resulting in some fraction of the mass being unavailable for desorption. For the Commerce soil, a degradation study meant to replicate batch conditions (results discussed below) indicated that about 4% of the applied GPS was fully mineralized at the beginning of desorption. This amount increased to around 23% following the timeframe of desorption. For the Sharkey soil, nearly 25% of the applied GPS was fully mineralized after the sorption experiments, which increased to 43% following desorption. Because full mineralization was demonstrated to occur but could only account for a fraction of the sorbed mass, both mineralization and GPS association with irreversible sites contributed to the low recovery during desorption.

Low recovery of the applied mass is in contrast to the results reported by Piccolo et al. (1994), where 15 to 80% of applied GPS was desorbed from their soil. However, input solution concentrations as well as soil/solution ratios were greater than those used in the present study, suggesting a possibility that increased loading of GPS resulted in association with lower affinity, and therefore more
reversible, sites. Furthermore, in the Piccolo et al. (1994) study, desorption commenced following only 2 h of reaction time for GPS sorption. This suggests that the propensity for GPS desorption from soils may be a function of reaction time. In accordance with our results, Maqueda et al. (2017) reported that only 0.4 to 1.22% of the applied GPS was recovered during three desorption steps following a 24-h sorption interval. Several other studies have also indicated limited desorption of GPS. Barrett and McBride (2007) indicated that up to 95% of applied GPS was retained in course-textured soil columns despite relatively high loading rates, and Kjær et al. (2005) reported complete retention of GPS and AMPA within a sandy soil during a 2-yr field trial.

Kinetic Modeling

Full sorption–desorption datasets for each input concentration were modeled using MRM. For the sake of applying a time-dependent retention model that assumes a conservative solute, any mass loss due to degradation of the herbicide in either the solution or sorbed phases is ignored. As such, parameter values were obtained based on solution concentrations determined by LSC and therefore do not discriminate between GPS and APMA, which are both 14C labeled. Consequently, parameter values presented here correspond to the sorption–desorption of GPS and AMPA as a whole. However, it has been shown that soils exhibit a similar affinity for both compounds (Báez et al., 2015), probably because both possess the highly reactive phosphonomethyl group. Therefore, optimized parameter values are expected to be valid for each compound individually as well as mixtures of the two. Observed data and MRM simulations using parameters generated from the combined adsorption and desorption datasets are shown in Fig. 3. Optimized parameter values are given in Table 2. Parameter values obtained from the simulation of single input

![Fig. 2. The 528-h sorption isotherm and desorption isotherms of glyphosate by Commerce and Sharkey soils. Error bars are the 95% confidence interval.](image)

![Fig. 3. Observed and multi-reaction model (MRM) simulated glyphosate adsorption and desorption in the Commerce and Sharkey soils. Error bars are the 95% confidence interval.](image)
The magnitudes of the rate coefficients suggest that sorption onto irreversible sites is more rapid than sorption onto reversible sites and an order of magnitude greater than desorption from reversible sites. This is consistent with the measured data, as sorption is highly limited. Optimized model parameters also suggest that rapid sorption is mainly attributed to reversible sites; however, secondary sorption and high retentive capacities of both soils are mainly attributed to irreversible sites. Although the performance of the MRM was improved as the input concentration was decreased, adjusted coefficients of determination for the overall set of parameters for both soils indicate a generally suitable description of the data (0.96 for Commerce and 0.97 for Sharkey).

Although the MRM performed reasonably well when describing the measured batch data, it is critical to acknowledge the limitations of the model. In the case of a nonconservative solute such as GPS, it is important to understand that the model cannot account for mass loss due to degradation. In terms of solution-phase GPS, this means that any decrease in solution concentration is accounted for by an increase in retention via a time-dependent reaction. In the actual system, decreases in solution concentration are brought about by both degradation and increased retention. Therefore, optimized rate coefficients associated with sorption reactions in both soils are probably overestimated. Additionally, it is expected that degradation of sorbed-phase GPS is significant (discussed below) and thus the model will also overestimate sorbed-phase concentrations.

### Glyphosate Dissipation

It is well documented in the literature that the phosphonic acid moiety is the most reactive functional group on the GPS molecule (Sprankle et al., 1975; Glass, 1987; Sheals et al., 2002; Gros et al., 2017). Therefore, GPS metabolites lacking this group are expected to be more mobile in the soil. Our results indicated that recovery of applied radioactivity during batch desorption was very low. This is indicative that $^{14}$C remained associated with the phosphonic acid moiety despite microbial degradation. Therefore, GPS degradation within the Commerce and Sharkey soils takes place mainly via the AMPA pathway, which is consistent with the findings of others (Borggaard and Gimsing, 2008; Sviridov et al., 2015). To determine the extent of degradation of solid-phase GPS, residual extracts were analyzed for the presence of both GPS and AMPA, with the results given in Table 3. Assuming that all radioactivity associated with the solid phase is attributed to either GPS or AMPA, 18 to 40 and 56 to 74% of sorbed GPS was metabolized to AMPA in the Commerce and Sharkey soils, respectively. It would appear that biological conditions within the Sharkey soil are more favorable for GPS degradation relative to the Commerce soil. According to Eberbach (1998), such results were unexpected because a high affinity of a soil for GPS should limit its bioavailability. Other studies have also indicated that lower rates of degradation in soils exhibiting higher affinities can probably be attributed to the limited bioavailability of sorbed-phase GPS (Al-Rajab and Schiavon, 2010; Zhelezova et al., 2017). In contrast, our results indicated that despite a higher affinity for GPS in the

### Table 2. Optimized multi-reaction model parameter values for kinetic sorption–desorption of glyphosate in Commerce and Sharkey soils.

<p>| Conc. GPS A MPA Fraction of GPS to AMPA |
|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Conc. mg L$^{-1}$</th>
<th>$k_{ss}$ h$^{-1}$</th>
<th>$k_1$ mg L$^{-1}$</th>
<th>$k_2$ mg L$^{-1}$</th>
<th>RMSE $^2$</th>
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<tr>
<td><strong>Overall</strong></td>
<td></td>
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<tr>
<td>1 0.049 ± 0.006</td>
<td>3.460 ± 0.265</td>
<td>0.230 ± 0.023</td>
<td>0.074</td>
<td>0.962</td>
</tr>
<tr>
<td>2 0.050 ± 0.014</td>
<td>1.845 ± 0.296</td>
<td>0.146 ± 0.031</td>
<td>0.006</td>
<td>0.934</td>
</tr>
<tr>
<td>5 0.050 ± 0.015</td>
<td>2.777 ± 0.474</td>
<td>0.166 ± 0.041</td>
<td>0.020</td>
<td>0.929</td>
</tr>
<tr>
<td>10 0.043 ± 0.015</td>
<td>2.872 ± 0.477</td>
<td>0.177 ± 0.042</td>
<td>0.056</td>
<td>0.923</td>
</tr>
<tr>
<td>20 0.039 ± 0.015</td>
<td>3.501 ± 0.731</td>
<td>0.234 ± 0.066</td>
<td>0.168</td>
<td>0.933</td>
</tr>
<tr>
<td><strong>Commerce soil</strong></td>
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<tr>
<td>1 0.045 ± 0.020</td>
<td>1.446 ± 0.247</td>
<td>0.137 ± 0.031</td>
<td>0.003</td>
<td>0.905</td>
</tr>
<tr>
<td>2 0.050 ± 0.014</td>
<td>1.845 ± 0.296</td>
<td>0.146 ± 0.031</td>
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<td>0.168</td>
<td>0.933</td>
</tr>
<tr>
<td><strong>Sharkey soil</strong></td>
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</tr>
<tr>
<td>1 0.065 ± 0.022</td>
<td>2.193 ± 0.409</td>
<td>0.071 ± 0.018</td>
<td>0.003</td>
<td>0.854</td>
</tr>
<tr>
<td>2 0.067 ± 0.019</td>
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<td>0.065 ± 0.013</td>
<td>0.005</td>
<td>0.899</td>
</tr>
<tr>
<td>5 0.060 ± 0.014</td>
<td>2.515 ± 0.570</td>
<td>0.071 ± 0.019</td>
<td>0.012</td>
<td>0.926</td>
</tr>
<tr>
<td>10 0.058 ± 0.013</td>
<td>2.436 ± 0.346</td>
<td>0.068 ± 0.013</td>
<td>0.024</td>
<td>0.937</td>
</tr>
<tr>
<td>20 0.059 ± 0.016</td>
<td>2.108 ± 0.199</td>
<td>0.066 ± 0.011</td>
<td>0.068</td>
<td>0.939</td>
</tr>
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</table>

† Mean ± 95% confidence interval.
Sharkey soil, microbial activity was dominant. This resulted in greater degradation in this soil than the Commerce soil. Several factors are associated with the rate and magnitude of GPS degradation, such as total microbial biomass (Franz et al., 1997; Rueppel et al., 1977) and the presence of specific microbial species (Gimsing et al., 2004b). Since GPS degradation in soils is mainly attributed to biotic processes (Sviridov et al., 2015), either general microbial activity is greater in the Sharkey soil or population dynamics are such that sorbed-phase GPS is more readily bioavailable.

To determine the fate of applied GPS in the batch studies, two mass balance calculations were performed. The first calculation accounted for only the mass recovered as GPS or AMPA in the batch sorption–desorption solutions as well as from the KOH extraction and ignored any degradation beyond AMPA. The reason for this approach is twofold. First, degradation of the applied GPS beyond AMPA was not monitored during the batch experiments, so any method of adjusting for mass lost this way is unavailable. More importantly, the MRM does not account for degradation, so this method of mass balance calculation was done as a validation of the final sorbed mass predicted by the model. The results of this first calculation are given in Supplemental Table S4. On average, mass recovery from the Commerce soil (85% of the applied mass) was much better than from the Sharkey soil (38% of the applied mass). This suggests that the assumptions of the MRM are more appropriate for the Commerce soil than for the Sharkey soil, indicating that the general performance of the model is soil dependent. Additionally, this provides a confirmation that the final sorbed-phase concentrations are overpredicted by the MRM.

Discrepancies in mass balances are attributed to incomplete extraction (<100%), as well as degradation of GPS beyond AMPA. The extraction method used here has been shown to have an efficiency of 86 to 100% (Miles and Moye, 1988), so it is believed that discrepancies are mainly the result of degradation. To confirm this, a separate degradation study was conducted. In contrast to traditional mineralization studies, the setup of this experiment was specifically meant to replicate the batch conditions. The results of this study are shown in Fig. 4. The average fraction of applied radioactivity (14C-GPS) recovered as 14CO2 was 43 and 23% from the Sharkey and Commerce soils, respectively. The second mass balance calculation is the application of these results to the first mass balance calculation. This resulted in improved average recoveries from the Sharkey and Commerce soils of about 80 and 100% of the applied mass, respectively, which are within the range of the KOH extraction method. The implications of this are that a model that also accounts for degradation will result in improved predictions of the sorbed mass at any given time.

The vast majority of GPS degradation studies reported rapid mineralization of the herbicide with no apparent lag time (Eberbach, 1998; Gimsing et al., 2004b; Al-Rajab and Schiavon, 2010; Yu et al., 2011), indicating that the metabolic pathways necessary for degradation were already present within the soil microflora. This is in contrast to the results given here, where there was an apparent lag time before greater rates of mineralization occurred. The observed lag times were approximately 8 d in the Sharkey soil and 15 d in the Commerce soil. Discrepancies between the results presented here and those reported previously are probably due to differences between the experimental designs. In previous experiments, water was applied to soils at a rate that generally resulted in a final moisture content less than saturation. In this case, microbes in the soil solution are concentrated and are in more direct contact with solvated or easily exchangeable GPS, resulting in the observed rapid mineralization. In our study, the 1:10 soil/solution ratio dilutes the antecedent microbial population. As such, a certain period of time was necessary for microbial activity or population density to increase such that considerable production of 14CO2 was observed. A first-order degradation model was fitted to the measured data, with the results given in Supplemental Table S5. Values of the optimized rate coefficient correspond to the GPS half-life of 59 and 161 d in the Sharkey and Commerce soils, respectively. The value for Sharkey is within the range of those reported by Zhelezova et al. (2017), whereas the Commerce half-life value is more similar to those attributed to the non-labile fraction of GPS estimated by Eberbach (1998). Again, caution must be used when comparing the results of this study to those reported previously, as considerable differences in methodology exist. These results serve to demonstrate that degradation beyond AMPA is significant in both soils and may partially explain discrepancies in mass balance calculations.

Conclusions

Kinetic batch studies of GPS sorption by Commerce and Sharkey soils indicate a high affinity of both soils for GPS, although Sharkey exhibited a greater affinity. Freundlich isotherms for both soils were generally characterized by nonlinearity at early sampling times but became more linear during the sorption experiments. The primary metabolite of GPS, AMPA, was detected in solution at various sampling times, indicating that
the degradation of GPS was significant during the batch studies. Because solution and sorbed-phase concentrations of GPS were not adjusted for the presence of AMPA, fitted Freundlich isotherms refer to the sorption of both compounds as a whole. Desorption studies indicate that GPS adsorption onto each soil can largely be considered an irreversible process, with only 2.3 to 3.4 and 1.9 to 2.5% of the applied GPS recovered from the Commerce and Sharkey soils, respectively. Low recoveries during desorption may be attributed to both irreversible sorption as well as degradation of sorbed-phase GPS. Sorption by both soils exhibited a time-dependent behavior, especially between 2 and 72 h of reaction time. The observed kinetics beyond 72 h may be partially attributed to degradation within the solution phase rather than additional sorption, especially for the Sharkey soil. A two-site MRM incorporating time-dependent reversible and irreversible reactions provided an adequate description of the kinetic batch data. Furthermore, the modeled results emphasize the dominance of irreversible type reactions in both soils. However, it is critical to acknowledge that the MRM does not account for degradation, and therefore values of the rate coefficients as well as sorbed-phase concentrations will probably be underestimated. Biological degradation of sorbed-phase GPS takes place mainly via the AMPA metabolic pathway and is more evident in the Sharkey than the Commerce soil. These results were further highlighted in a subsequent degradation study, where 43 and 23% of applied GPS radioactivity was recovered as 14CO2 from the Sharkey and Commerce soils, respectively. To improve predictions of the behavior and fate of GPS in soils, future models should account for time-dependent reactions as well as degradation in both solution and sorbed phases.

Supplemental Material
The supplemental material includes additional information about soil properties, UPLC-MS/MS analysis, and the experimental design of the degradation studies. It also includes the results of mass balance calculations along with fitted degradation coefficients and their corresponding half-life values.

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References


