Environmental Fate and Behavior of the Herbicide Glyphosate in Sandy Soils of Florida Under Citrus Production

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Chemical weed control using herbicide glyphosate to manage emerged weeds is an important production practice in Florida citrus. Despite the extensive use of glyphosate in citrus orchards, very limited information is available on its environmental fate and behavior in Florida soils that are predominantly sandy in nature. Hence, the study's objective was to understand the adsorption-desorption, dissipation dynamics, and vertical movement or leaching of glyphosate in sandy soils in citrus orchards. Laboratory, field, and greenhouse experiments were conducted at Southwest Florida Research and Education Center in Immokalee, Florida. The adsorption-desorption behavior of glyphosate in the soils from three major citrus production areas in Florida was studied utilizing a batch equilibrium method. The dissipation of glyphosate was tracked in the field following its application at the rate of 4.20 kg ae ha^{-1}. Soil leaching columns in greenhouse conditions were used to study the vertical movement of glyphosate. The results suggest that glyphosate has a relatively lower range of adsorption or binding (K_{ads} = 14.28–30.88) in the tested soil types. The field dissipation half-life (DT_{50}) of glyphosate from surface soil was found to be ~26 days. Glyphosate moved vertically or leached into the soil profile, up to 40 cm in the soil column, when analyzed 40 days after herbicide application. The primary degradation product of glyphosate, i.e., aminomethyl phosphonic acid (AMPA), was also detected up to the depth of 30 cm below the soil surface, indicating the presence of microbial metabolism of glyphosate in the soil.

Keywords: adsorption, desorption, dissipation, half-life, leaching

INTRODUCTION

Ever since the recognition of its phytotoxic activities in 1970s, glyphosate has been regarded as a relatively safe herbicide in the environment because it is quickly inactivated in the soil by adsorption and degradation (Quinn et al., 1988; Cuhra et al., 2016). However, prior reports have also indicated that improper application practices and excessive use of this herbicide may potentially contribute to its non-target movement and consequent effects in aquatic and terrestrial environments (Borggaard and Gimsing, 2008; Hanke et al., 2010; Cederlund and Cheng, 2017). Besides the direct sprays, glyphosate's exposure routes in the environment may also include decaying plant residues and

exudation from roots of sprayed plants (Neumann et al., 2006; Mamy et al., 2016), which is especially the case for genetically modified, glyphosate-tolerate crops with a high level of accumulated glyphosate (Bøhn et al., 2014). Furthermore, the adoption of agriculture crops with genetically introduced tolerance to glyphosate indirectly increases the risk of its excessive and non-judicious use of this herbicide in crop production, thereby raising more environmental and crop safety implications worldwide (Kanissery et al., 2019). Among these environmental concerns related to glyphosate, its persistence and movement within the soil profile and its effects on non-target components of the crop ecosystem have received the most attention and are deemed one of the most important factors to be addressed by scientific research.

The major pathway for glyphosate's dissipation from the soil is microbial-mediated transformation or biodegradation (Sprankle et al., 1975; Torstensson, 1985; Gimsing et al., 2004b; Okada et al., 2019). Glyphosate may also be transported to groundwater, surface water, and water-sediment by processes like surface runoff, erosion, drift, and leaching (Newton et al., 1994; Ellis and Griffin, 2002; Shushkova et al., 2010; Bott et al., 2011; Lupi et al., 2015). Major factors that affect glyphosate's persistence and movement in the soils include soil pH, soil type, mineralogy, texture, organic matter content, soil nutrient status, and surface vegetation cover (De Jonge et al., 2001; Laitinen et al., 2006; Mamy et al., 2016). Glyphosate-soil interaction occurs by processes such as adsorption and desorption; while both processes play important roles in determining the availability, persistence and movement of the herbicide in soil, relatively fewer studies have been conducted to evaluate the movement and environment fate in a noncontrolled environment (Borggaard and Gimsing, 2008; Aparicio et al., 2013). Understanding the topics of glyphosate-soil interactions will allow more informed usage of glyphosate as an effective, crop- and environmentally safe weed management tool.

Florida's citrus-producing areas have soils with unique properties, characterized by very low organic matter content, sandy soil texture, low water holding capacity, etc. For instance, Immokalee and Fort Pierce, the major citrus production areas in southwest and southeast Florida, respectively, have poorly drained sandy soils with high water tables, whereas Lake Alfred, in the central production area, is known for its extremely well-drained sandy soils with low water holding capacity (Obreza and Collins, 2008; Obreza and Morgan, 2008). Although glyphosate is an extensively used herbicide in citrus weed management in the state (USDA, 2018), scarce information is available on the herbicide's fate and behavior in these soils. Hence, it is imperative to understand how glyphosate binds, persists and moves in Florida's soils to improve its utilization in citrus weed management. To address this need, we evaluated the adsorption and desorption pattern of glyphosate in soils from three major citrus-producing areas (southwest, southeast, and central) of Florida in a laboratory study. Moreover, field and soil column studies were conducted in southwest Florida soil to characterize glyphosate dissipation and movement.

MATERIALS AND METHODS

Adsorption-Desorption Study
Soil Collection
The soils used for this study were collected from citrus orchards in three major citrus-producing areas with similar sandy soil types in Florida: southwest (Location: Immokalee; latitude: 26°28′7″N, longitude: 81°26′26′22″W), southeast (Location: Fort Pierce; latitude: 28°26′6′7″N, longitude: 81°26′41′35″W) and central (Location: Lake Alfred; latitude: 2726°26′7″N, longitude: 80°26′25′25″W). Soils without a history of glyphosate application in the past 2 years were chosen in each sampling location. Soils were collected from the top layer (15 cm depth) at five different sampling points in a transect fashion, and each of these three locations is treated as a spatial replicate. Following the collection, a composite sample for each location was prepared by mixing all the subsamples and was stored at -20 °C until the experiment. The soil samples were air-dried, sieved through a 2-mm mesh before use in experiments. The relevant physico-chemical properties of the soils are provided in **Table 1** (Analysis by Waters Agricultural Laboratories, Camilla, GA).

Chemicals and Reagents
The analytical standard (99.99% purity) of glyphosate in water (1,000 mg L^{-1}) was procured from Restek (Bellefonte, PA, United States). Five different concentrations (5, 10, 25, 50, and 100 mg L^{-1}) of glyphosate were prepared in 0.1 M (M) potassium chloride (KCl) solution in water (Gimsing and Borggaard, 2001). All the chemicals, reagents and solvents used in this experiment were of analytical grade and obtained from Fisher Scientific (Pittsburgh, PA).

Experimental Protocol
The methodology for determining adsorption isotherms was established according to the adsorption/desorption batch equilibrium study in the environmental protection agency's test guidelines (USEPA, 2008). A preliminary study based on these guidelines was carried out to determine the optimum soil/solution ratio for this experiment and is provided in the supplemental information (**Supplementary Table S1**; **Supplementary Figure S1**). As suggested by the preliminary study (1:5 soil/solution ratio), 4 g of air-dried soil were weighed and equilibrated with 20 ml of glyphosate test concentrations (5, 10, 25, 50, and 100 mg L^{-1}), prepared in 0.1 M KCl solution. The soil was shaken with the glyphosate solutions in 40 ml Teflon centrifuge tubes with a threaded cap on a horizontal shaker (200 rpm) for 24 h (Accinelli et al., 2005). The likelihood of significant degradation of glyphosate during this contact time (24 h) with soil during the shaking is assessed to be negligible previously (Bergström et al., 2011). The study was conducted in duplicate for each soil type and each concentration in a semi-dark room with a controlled temperature of 25 ± 2 °C. At the end of shaking time, following the equilibration of soil and glyphosate solution, the resultant soil suspension in the tubes was centrifuged at 6,000 rpm for 15 min. Subsequently, after

TABLE 1 | Selected physical and chemical properties of the citrus production soils (top 15 cm) used in this study.

Soil properties	Soil / Location		
	Immokalee (southwest FL)	Fort pierce (southeast FL)	Lake alfred (central FL)
Soil type	Sand	Sand	Sand
Sand[a] (%)	95.8	94.8	90.0
Silt + Clay[a] (%)	7.2	5.2	10.0
Phosphorus[b] (kg ha^{-1})	76.2	70.6	291.4
Soil pH	6.1	6.0	5.9
Organic matter[c] (%)	0.73	0.44	0.59
CEC[d] (meq 100g^{-1})	5.0	2.8	4.0

[a]Determined by hydrometer method.
[b]Determined by Mehlich III method.
[c]Determined by loss of ignition.
[d]Cation exchange capacity.

centrifugation, two 1-ml aliquots were taken from the supernatant of each sample. The glyphosate concentration in each aliquot of aqueous soil solution was determined by high-performance liquid chromatography-mass spectrometry (HPLC-MS) at Southwest Florida Research and Education Center (SWFREC), Immokalee, FL. The HPLC-MS conditions for analysis of glyphosate in an aqueous solution are provided as supplemental information (**Supplementary Table S2**). The limit of detection for glyphosate in the analysis was 500 µg L^{-1}. Two blanks (treatments without glyphosate) and controls (treatment without soil) for each concentration and soil type were also included in the study for calibration and background correction process. Background glyphosate content was not detected in any test soils (**Supplementary Table S3**), and significant adsorption of glyphosate on the tubes was not observed (**Supplementary Table S4**). The amount of herbicide adsorbed to the soil was determined by calculating the difference between herbicide concentration in the aqueous soil solution at equilibrium and initial concentration in the shaking solution.

Following the adsorption experiment, the desorption of glyphosate from soils was determined. The supernatant from the adsorption study was removed, and an equal amount (20 ml) of fresh 0.1 M KCl solution was added again to each Teflon tube. Soil aggregates were dispersed by vibration, and the contents of all the tubes were homogenized on a horizontal table shaker for 24 h at 200 rpm. Following re-equilibration, the Teflon tubes were centrifuged (15 min, 6,000 rpm), and 1 ml aliquots of the supernatant were pipetted into plastic vials in duplicates. The supernatants were then analyzed for glyphosate concentration by HPLC-MS. The desorbed amounts were calculated by analyzing the amount of herbicide in the aqueous solution following equilibration.

Field Dissipation Study
Experimental Design and Treatments
The dissipation of glyphosate was determined concurrently from a field experiment evaluating glyphosate effects on young citrus trees in a newly established citrus orchard located at SWFREC, Immokalee, Florida. The experiment had a randomized complete block design (RCBD) with four replications. Each replication

(experimental plot) consisted of five young trees. One tree was left as a buffer between experimental plots. The experimental site did not have any prior application history of glyphosate-based herbicide products. For this study, herbicide was applied once during the fall season of 2018. The treatments consisted of glyphosate applied at 4.20 kg ae ha^{-1}, which is within the recommended range of glyphosate rates in citrus (University of Florida, 2020) and an untreated control consisting of water spray.

Herbicide Application and Orchard Management
The herbicide spray solutions were made by mixing the appropriate amount of glyphosate product (Roundup custom™, 53.8% glyphosate in the form of its isopropylamine salt, EPA registration number 524–343) in distilled water according to manufacturer recommendation. The carrier volume selected was 280 L ha^{-1}. Herbicide solution was applied using a handheld backpack sprayer to the tree rows, i.e., roughly one square meter around each tree. Weed pressure was minimal around trees during the application. For nutrition, irrigation, disease, and pest management, recommended orchard management practices were followed throughout the study (University of Florida, 2020). The citrus trees received homogenous irrigation with the micro-sprinklers twice a week for 2 h each day. The daily rainfall data were obtained from the Florida automated weather network (FAWN) weather station at SWFREC.

Soil Sampling and Analysis
The soil was sampled from the top 15 cm depth at pre-determined intervals (0, 7, 14, 28, 42, 56, 70, and 90 days after treatment) beginning from the first day after herbicide application. The soil samples were immediately stored at -20°C after sampling until analysis of the soil samples for glyphosate. For assessing the field dissipation kinetics, soil samples from the experimental plots collected at different time points were analyzed for herbicide content. To reduce the analytical costs, a total of two composite samples for each time point were formed by combining the soil samples from four replications before the analysis (USEPA, 1995). The analysis
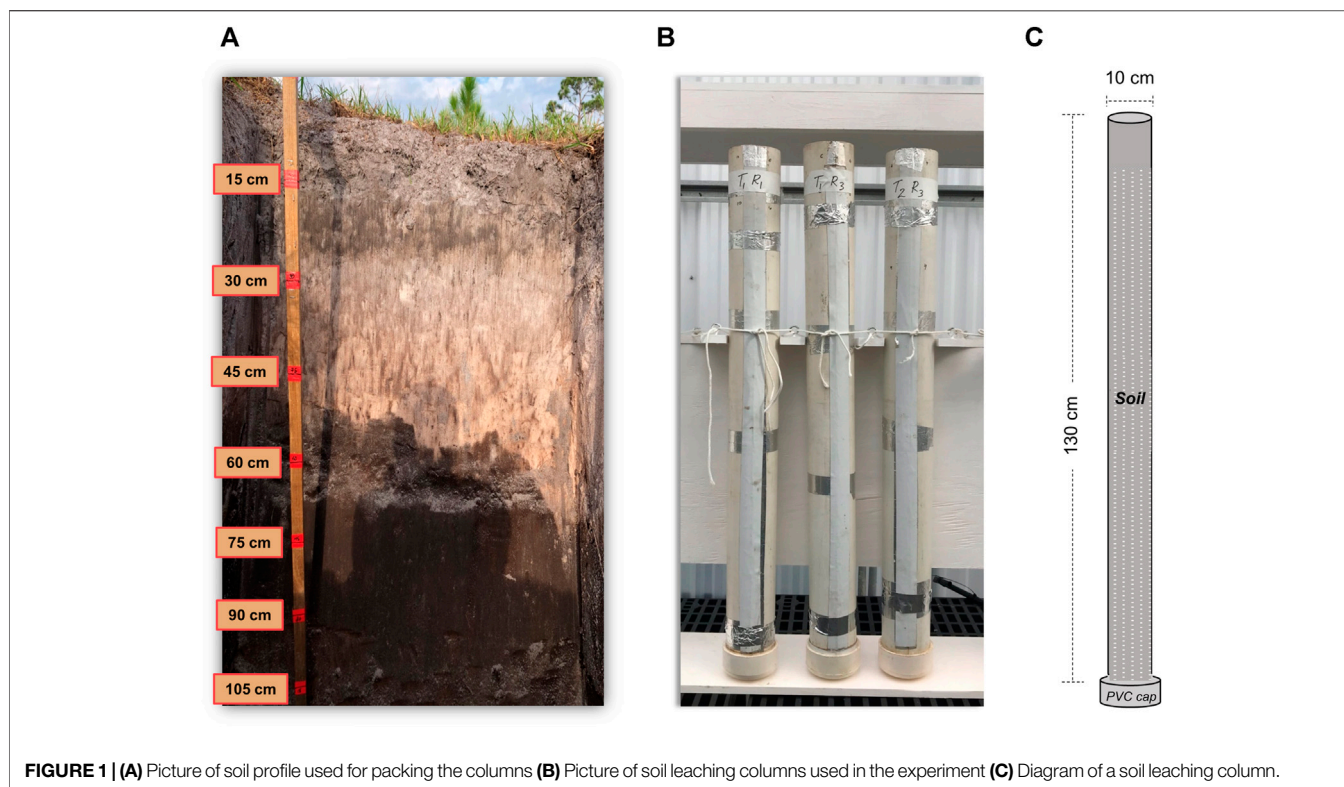
FIGURE 1 | (A) Picture of soil profile used for packing the columns **(B)** Picture of soil leaching columns used in the experiment **(C)** Diagram of a soil leaching column.

of glyphosate content in the soil samples was performed using HPLC-MS/MS in a commercial laboratory (Waters Agricultural Laboratories, Camilla, GA). Glyphosate was extracted from the soil samples, and analysis was conducted utilizing methods described in Gorica et al., 2016. The method detection limit for glyphosate was 50 µg kg^{-1} soil.

Soil Column Leaching Study
Column Preparation
Soil leaching columns (130 cm in length, 10 cm in diameter) made of polyvinyl chloride (PVC) pipes were set up in the greenhouse at SWFREC. The columns were filled with pre-collected soil from the incremental depths (up to 120 cm) from a site (without prior glyphosate application history) adjacent to a citrus orchard in Immokalee to mimic the soil depth profile of the orchard (**Figure 1A**). The column was fitted with a PVC cap at the bottom, equipped with a nylon screen and Whatman no. 4 filter paper to collect the leachate, if any. The columns were secured upright in a specially prepared wooden stand (**Figures 1B,C**), and each column was watered to field capacity and allowed to drain for 24 h.

Experimental Design and Treatments
The experiment was set up in a completely randomized design (CRD) with three replications. The treatments consisted of glyphosate application (4.20 kg ae ha^{-1}) and untreated control (water spray). Control was included for background correction purposes. Glyphosate (Roundup Custom$^{™}$) was mixed thoroughly in deionized water (carrier volume = 280 L ha^{-1}) to

prepare the herbicide solutions and applied with a handheld CO_2 backpack sprayer to the soil surface in the soil column. The frequency and volume of water being added to a citrus orchard per unit area through irrigation were calculated and applied to the column regularly (two times a week) to simulate field irrigation. The soil columns were kept intact until sampling (for 40 days).

Sample Collection and Analysis
After 40 days, the PVC cap at the end of the soil column was removed, and the columns were split longitudinally by removing the duct tape from one side. The soil in the columns was collected in an interval of 10 cm depths for the column's entire length. The collected soil samples were analyzed for parent herbicide, glyphosate, and its primary metabolite aminomethylphosphonic acid (AMPA) content using HPLC-MS/MS (Gorica et al., 2016) in a commercial laboratory (Waters Agricultural Laboratories, Camilla, GA). The method detection limit for glyphosate and AMPA were 50 and 120 µg kg^{-1} soil, respectively.

Data Analysis
The adsorption and desorption isotherms were fitted using the transformed Freundlich isotherm equation: log Cs = log K$_f$ + 1 / n log Ce, where "Cs" is the concentration of glyphosate adsorbed in the soil (mg kg^{-1}), K$_f$ is the equilibrium constant of Freundlich reflecting the binding affinity of the soil for the herbicide, 'Ce' is the concentration of glyphosate in the solution (mg L^{-1}) at equilibrium, and 1/n is the degree of linearity of the isotherm. The K (intercept) and 1/n (slope) were calculated using regression analysis in the adsorption and desorption isotherms.

FIGURE 2 | Freundlich adsorption isotherm plots of glyphosate in Florida's citrus production soils.
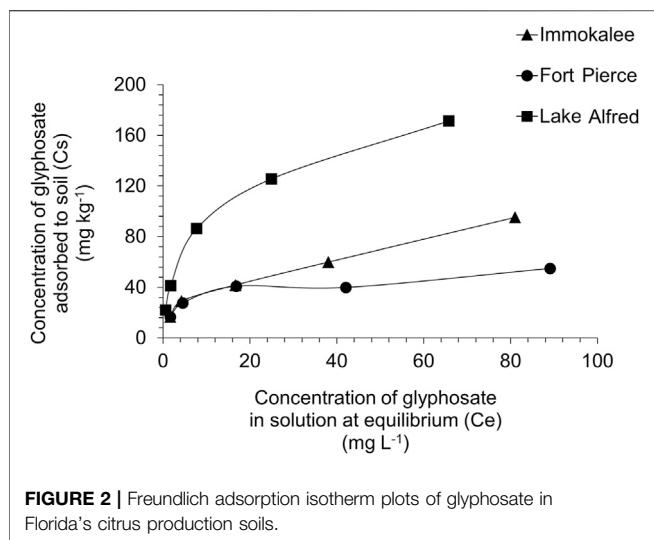
The field dissipation data of glyphosate in soils were fitted into the first-order kinetics model $C_t = C_0\, e^{-kt}$ where 'C_0" is the initial concentration ($\mu g\, kg^{-1}$ soil) of the herbicide in the soil, "C_t" is the herbicide concentration ($\mu g\, kg^{-1}$ soil) detected in the soil at time t, and k is the first-order rate constant. Computer Assisted Kinetic Evaluation (CAKE) (version 3.3; Tessella, Newton, MA) software was utilized to model the dissipation kinetics and estimate the first-order dissipation parameters.

PROC GLM statement in SAS (version 9.4; SAS Institute, Cary, NC) software was used for the analysis of variance (ANOVA), and mean separation was achieved using Tukey's HSD test at $p \le 0.05$.

RESULTS AND DISCUSSION

Adsorption-Desorption Study

For the range of herbicide concentrations (5–100 mg L^{-1}) and soils, adsorption data from the current experiment were well-fitted into the Freundlich isotherm model ($R^2 > 0.91$). **Figure 2** demonstrates the adsorption isotherm plots, and **Table 2** shows the calculated Freundlich adsorption coefficient (K_{ads}), slope (1/n_{ads}), and the corresponding goodness of fit (R^2) for glyphosate adsorption in various soil types tested. Among the different soils, the slope (1/n_{ads}) values ranged from 0.27 to 0.43, and the Freundlich adsorption coefficient (K_{ads}) values ranged from 14.3 to 30.9. A lower K_{ads} value indicates a low adsorption affinity of the soil to the herbicide. The soil from Lake Alfred location showed a significantly higher ($p \le 0.05$) adsorption coefficient than the soils from Immokalee and Fort Pierce. The adsorption coefficients for Immokalee and Fort Pierce soil were found to be similar (**Table 2**).

Desorption isotherms for glyphosate in all the soils also fitted into the Freundlich model ($R^2 > 0.84$) (**Table 2**). Freundlich desorption coefficient (K_{des}) values of glyphosate were considerably lower in the Immokalee and Fort Pierce soils than the Lake Alfred soil. A lower K_{des} value indicates lesser

retention of herbicide on the soil surface, and consequently, higher release into the soil solution.

The adsorption parameter, K_{ads}, observed in the current study, agrees with the previous observation from similar soil types, where glyphosate had a K_{ads} of 34.5 in sandy loam soil (Al-Rajab et al., 2008). The results obtained from the adsorption-desorption study are in the lower range of K_{ads} and 1/n values obtained for glyphosate from different soil types and crop production systems. There is a large variation in the literature values, with K_{ads} ranging from 0.6 to 5.0 x 10^5 and 1/n ranging from 0.26 to 1.26 (Vereecken, 2005). This variability in glyphosate adsorption is attributed to soils' physical and chemical heterogeneity (Al-Rajab et al., 2008). The lower adsorption values of glyphosate obtained from the present study indicate lower soil adsorption affinity of this herbicide in all three citrus-producing locations. Clay and organic matter content of soils tend to affect glyphosate adsorption positively (Vereecken, 2005). The citrus growing soils in Florida are predominantly sandy (>90% sand) and low in organic matter (Obreza and Collins, 2008) and could be a plausible reason behind relatively lower adsorption and higher desorption of glyphosate in these soil types. Soil organic matter (SOM) seems to play a questionable role in soil adsorption of glyphosate. On the one hand, investigations have shown that soil sorption of glyphosate is positively correlated with SOM content (Piccolo et al., 1996). However, there are reports that it sometimes negatively impacts glyphosate adsorption to soil (Gimsing et al., 2004a).

Also, it has to be noted that adsorption was comparatively higher in soil from Lake Alfred compared to the Immokalee and Fort Pierce soils. Lake Alfred soil has more silt and clay, and phosphorus (P) than the other two soils tested in this study (**Table 1**). Although most herbicides, due to their non-polar functional groups, are adsorbed in soils primarily by SOM, glyphosate, a small molecule with three polar functional groups (carboxyl, amino and phosphonate groups), is strongly adsorbed by soil minerals (Borgaard and Elberling, 2007). Hence, clay minerals like iron (Fe) and aluminum (Al) oxides in the soil can provide binding or adsorption sites to the glyphosate (Gimsing and Borggaard 2002; Kanissery et al., 2015). Likewise, sand particles coated with Fe and Al sesquioxides (also known as 'coated sands') have been found to improve P adsorption and retention in Florida soil (Obreza and Collins, 2008). It is well known that glyphosate and phosphate are structurally analogous and share similar adsorption mechanisms in soil (Gerritse et al., 1996; Gimsing and Borggaard 2001; Wang et al., 2005). The active phosphonate end group in the glyphosate molecule allows it to form inner-sphere complexes on Fe and Al oxide surfaces (Gimsing and Borggaard 2002; Sheals et al., 2002). Hence, significantly higher amounts of phosphorus observed in the Lake Alfred soil (**Table 1**) could be an indication of better availability of adsorption sites in that soil, owing to the presence of coated sands, and could be a probable reason behind the higher adsorption of glyphosate in this particular soil.

The value of slope (1/n) < 0.5 in the adsorption model (**Table 2**) indicates a strong non-linear relationship between the amount of herbicide adsorbed onto the soil surface and its

TABLE 2 | Adsorption and desorption (Freundlich model) parameters of glyphosate in Florida's citrus production soils.

Soil / Location	Freundlich coefficient		Isotherm slope		R^{2e}	
	Adsorption (K_{ads}[a])	Desorption (K_{des}[b])	Adsorption ($1/n_{ads}$[c])	Desorption ($1/n_{des}$[d])	Adsorption	Desorption
Immokalee	14.28[f] (±0.83) B[g]	13.30[d] (±1.5) B	0.41 (±0.01)	0.42 (±0.06)	0.98	0.84
Fort Pierce	16.56 (±0.17) B	17.88 (±1.8) B	0.27 (±0.01)	0.58 (±0.08)	0.91	0.84
Lake Alfred	30.88 (±0.82) A	38.51 (±1.4) A	0.43 (±0.04)	0.70 (±0.02)	0.98	0.97

[a]K_{ads} Freundlich adsorption coefficient.
[b]K_{des} Freundlich desorption coefficient.
[c]$1/n_{ads}$ Adsorption isotherm slope.
[d]$1/n_{des}$ Desorption isotherm slope.
[e]R^2 Goodness of fit for the Freundlich model.
[f]Mean ± 95% Confidence Interval.
[g]Letters beside the numeric values indicate Tukey's HSD at $p \leq 0.05$. Values with the same letters in a column are not significantly different.

TABLE 3 | First-order field dissipation parameters of glyphosate in a citrus orchard (Location: Immokalee, FL).

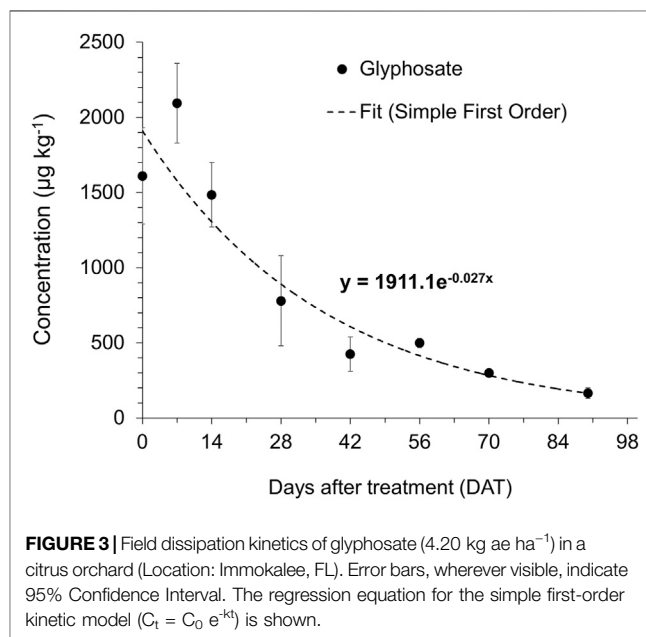| First-order parameters	Value
DT_{50}[a] (days)	25.9[e] (±2.74)
DT_{90}[b] (days)	86.0 (±8.82)
k[c] (day^{-1})	0.026 (±0.002)
R^{2d}	0.88 (±0.15)

[a]DT_{50} Dissipation Half-life or 50% dissipation time.
[b]DT_{90} 90% dissipation time.
[c]k Rate constant.
[d]R^2 Goodness of fit for simple first-order kinetic model.
[e]Mean ± 95% Confidence Interval.

FIGURE 3 | Field dissipation kinetics of glyphosate (4.20 kg ae ha^{-1}) in a citrus orchard (Location: Immokalee, FL). Error bars, wherever visible, indicate 95% Confidence Interval. The regression equation for the simple first-order kinetic model ($C_t = C_0 e^{-kt}$) is shown.

concentration in the aqueous solution. The result indicates that less glyphosate will be adsorbed in the soil as the glyphosate concentration in the solution increases, possibly because most of the adsorption sites are bound to glyphosate, and fewer sites are available for adsorption. This observation suggests a high potential for glyphosate leaching when higher concentrations of this herbicide are present in the soil profile.

Soils with a lower adsorption affinity showed greater desorption, as evident by the K_{des} value (**Table 2**). Higher desorption or release of glyphosate from Immokalee and Fort Pierce soils suggests that the herbicide's mobility for leaching losses or its availability for biodegradation and plant uptake in these soils will be higher. The relatively lower desorption in the Lake Alfred soil suggests that glyphosate will be less mobile and more bound to this soil than the other two citrus production soils tested. Generally, glyphosate is non-bioavailable and inactive when bound or adsorbed to soils (Sorensen et al., 2006).
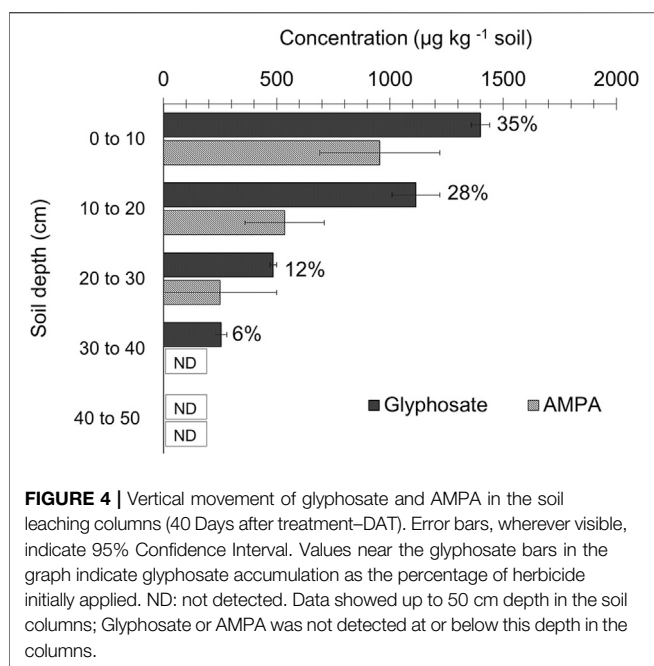
Field Dissipation Study

The dissipation parameters of glyphosate obtained from the field study conducted in Immokalee, FL, are presented in **Table 3**. The dissipation of glyphosate from the surface soil (top 15 cm) over time (**Figure 3**) adequately fitted into a first-order kinetic model with an R^2 value of 0.88. The first-order rate constant (k) value was 0.026 days^{-1}. The dissipation half-life (DT_{50}: time for dissipating 50% of initially applied herbicide from the soil) of glyphosate from the surface soil was 25.9 days. The time for dissipating 90% of initial herbicide (DT_{90}) was 86 days. The cumulative amount of precipitation received in the

experimental site during the dissipation study duration is shown in the supplemental materials (**Supplementary Figure S2**).

The half-life of glyphosate applied in the field (~26 days) was well within the range of half-lives in similar soil types reported previously (Okada et al., 2019); between 9 and 38 days. Glyphosate DT_{50} can vary from a few days to months and even years, depending upon several factors, including soil type, texture, organic matter content and other soil environmental conditions (Sprankle et al., 1975; Nomura and Hilton 1977; Carlisle and Trevors 1988). The glyphosate dissipation was well-fitted and described using first-order kinetics, showing rapid initial dissipation of glyphosate followed by a decreased glyphosate dissipation rate which are in agreement with previously conducted research (Mamy et al., 2005; Bergström et al., 2011; Ghafoor et al., 2011). Interestingly, the detected concentration of glyphosate peaked at 7 days after application and then began to decline. A similar observation was made by (Salazar López et al., 2016), where glyphosate concentrations reached a maximum in soil 10–18 days after application.

FIGURE 4 | Vertical movement of glyphosate and AMPA in the soil leaching columns (40 Days after treatment–DAT). Error bars, wherever visible, indicate 95% Confidence Interval. Values near the glyphosate bars in the graph indicate glyphosate accumulation as the percentage of herbicide initially applied. ND: not detected. Data showed up to 50 cm depth in the soil columns; Glyphosate or AMPA was not detected at or below this depth in the columns.

Although the bulk of the applied glyphosate quickly dissipated from the soil surface in the current study, traces of herbicide could remain in the top 15 cm layer almost 3 months after the application, as noted from a prolonged DT_{90}. Researchers have reported a DT_{90} of over 7 months for glyphosate in certain cases, particularly when the soils are rich in silt and clay content (Okada et al., 2019).

Dissipation of herbicides from the soil can occur through microbially or chemically mediated transformations, surface or subsurface runoff, and leaching. Physico-chemical processes like adsorption and leaching in the soil and microbial degradation are considered primary determinant factors for the glyphosate dissipation from the applied area (Laitinen, 2009). The relatively lower adsorption affinity of glyphosate to sandy soils in citrus orchards in Florida observed from the current study could be potentially implied as a reason behind the quick dissipation of glyphosate, owing to its enhanced mobility from the soil surface.

Soil Column Leaching Study

Figure 4 shows the vertical leaching of glyphosate at different depths in the soil columns. Glyphosate was detected up to 40 cm below the surface in the soil profile columns when they were opened and analyzed 40 days after the herbicide application. The primary degradation product of glyphosate, AMPA, was also detected up to the depth of 20–30 cm below the soil surface. About 35% of applied glyphosate was retained in the top 0–10 cm, and 28% of applied herbicide was found accumulated in the 10–20 cm soil layer, and ~81% of the initially applied glyphosate was detected within a soil depth of 40 cm in the column. Glyphosate was not detected from the samples beyond 40 cm deep from the herbicide-treated columns or any depth samples in untreated control columns. Analysis of leachate for herbicide

content was not performed as only an insignificant amount of leachate was collected at the column's bottom cap. Also, leachate was observed to be turbid and brownish resulting from soil colloids.

Glyphosate has moved vertically up to 40 cm in the soil, as observed from soil columns. A similar trend was observed by Laitinen. (2009), who found glyphosate's movement up to 35 cm in a soil profile, 38 days after the herbicide application. The loss of mass balance of glyphosate in the soil columns (recovery from various depths accounts for 81% of the initially applied amount) in the current study could be attributed to the herbicide's microbial transformation. The primary metabolite AMPA was detected at various soil depths in the columns (**Figure 4**). Most citrus-producing soils in Florida, including the Immokalee soil used in this column study, have low soil organic matter (SOM) (**Table 1**). As SOM is closely linked to soil microorganisms, the potential for microbial transformation of herbicides is expected to be relatively low in these soils. However, the detection of AMPA in our soil columns, the most common product of glyphosate's microbial metabolism (Dick and Quinn 1995), indicates the presence of microbial transformation as a contributing mechanism for glyphosate dissipation and loss from the citrus orchards.

Only 35% of the applied glyphosate stayed in the top 10 cm in the column, followed by relatively lower concentrations in the subsequent soil depths. The vertical movement of glyphosate through the soil profile could be associated with its hydrophilicity and high-water solubility. The soil type utilized for this column study (Immokalee soil) is notably very sandy (>90% sand) with low clay content characterized by lower herbicide retention. Therefore, this may have promoted glyphosate leaching from the surface soils, especially when coupled with simulated citrus tree irrigation in the soil columns. On the other hand, the soils from this location have poor drainage properties due to a subsurface organic hardpan (Obreza and Collins 2008) that possibly restricted the downward movement of the herbicide (>40 cm) into deeper soil layers. Comparable reports on relatively low leaching and mobility of glyphosate have been reported from a previous study conducted in sandy soils. Researchers attribute this to the strong adsorption of glyphosate to soils. Furthermore, degradation of glyphosate to its major metabolite, AMPA, was also observed in the studied soil (Zhou et al., 2010). High rates of glyphosate leaching will be expected in tropical sandy soils like citrus production soils in FL due to their low adsorption capacity and relatively high precipitation. However, field investigations and column studies have shown that physical properties, like porosity, compaction etc., greatly determine the mobility of glyphosate in these soils. For instance, Kjær et al., 2005 showed minimal leaching of glyphosate (or AMPA) in sandy soils and is attributed to the absence of macropores in these soils. Sandy soils in the tropics offer a wide range of such properties (Bruand et al., 2005) and must be considered while predicting the leaching and movement of glyphosate in such soils. The fact that the citrus tree root zone in these types of soils generally occurs within 0–45 cm (Leiva et al., 2015) entails further investigations into the retention of this herbicide in the citrus root zone for an extended period, thus

enabling the uptake of its residues by roots (Cornish and Burgin, 2005; Tong et al., 2017).

CONCLUSION

Glyphosate was found to have low adsorption or binding affinity to the soils from all three citrus-producing locations in Florida. Among the various production areas, soil from Lake Alfred in the central area had higher adsorption for glyphosate than the other two areas, Immokalee in the southwest and Fort Pierce in the southeast. Field dissipation of glyphosate from surface soils in citrus orchard was relatively fast, with a calculated DT_{50} of ~26 days. The herbicide moved vertically from the surface soils up to 40 cm in soil profile columns within 40 days after herbicide application. The current study is among the first attempts to evaluate glyphosate's interaction with FL sandy soils under citrus production to the best of our knowledge. The information generated in this study could be utilized to better understand glyphosate's fate and behavior in citrus and other similar production systems in sandy soils. Additionally, these observations may be used to improve glyphosate's crop-safe application while minimizing the non-target effects and other environmental implications. Due to the low adsorption of glyphosate observed in citrus soils of FL, the likelihood of its availability to reach unintended areas in citrus orchards through processes such as leaching and surface runoff is relatively high. Although found to dissipate relatively quickly from the topsoil following application, its potential to persist in the deeper layers of soils and consequent interaction with the citrus tree needs to be explored more thoroughly. Being the most widely used herbicide

in citrus production in the region, findings from this study entail adopting glyphosate's judicious utilization to enhance its use as a weed control tool in citrus production.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

Conceptualization, RK and BG; Methodology, BG and RK; Investigation, BG; Resources, RK; Writing–Original Draft Preparation, BG; Writing–Review and Editing, RK, WL, OB, PD, and DK; Supervision, RK; Project Administration, RK; Funding Acquisition, RK.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fenvc.2021.737391/full#supplementary-material

REFERENCES

Accinelli, C., Koskinen, W. C., Seebinger, J. D., Vicari, A., and Sadowsky, M. J. (2005). Effects of Incorporated Corn Residues on Glyphosate Mineralization and Sorption in Soil. *J. Agric. Food Chem.* 53 (10), 4110–4117. doi:10.1021/jf050186r

Al-Rajab, A. J., Amellal, S., and Schiavon, M. (2008). Sorption and Leaching of 14C-Glyphosate in Agricultural Soils. *Agron. Sustain. Dev.* 28 (3), 419–428. doi:10.1051/agro:2008014

Aparicio, V. C., De Gerónimo, E., Marino, D., Primost, J., Carriquiriborde, P., and Costa, J. L. (2013). Environmental Fate of Glyphosate and Aminomethylphosphonic Acid in Surface Waters and Soil of Agricultural Basins. *Chemosphere* 93 (9), 1866–1873. doi:10.1016/j.chemosphere.2013.06.041

Bergström, L., Börjesson, E., and Stenström, J. (2011). Laboratory and Lysimeter Studies of Glyphosate and Aminomethylphosphonic Acid in a Sand and a clay Soil. *J. Environ. Qual.* 40 (1), 98–108. doi:10.2134/jeq2010.0179

Bøhn, T., Cuhra, M., Traavik, T., Sanden, M., Fagan, J., and Primicerio, R. (2014). Compositional Differences in Soybeans on the Market: Glyphosate Accumulates in Roundup Ready GM Soybeans. *Food Chem.* 153, 207–215. doi:10.1016/j.foodchem.2013.12.054

Borggaard, O. K., and Elberling, B. O. (2007). *Pedological Biogeochemistry.* Department of Natural Sciences, University of Copenhagen and Department of Geography and Geology, University of Copenhagen.

Borggaard, O. K., and Gimsing, A. L. (2008). Fate of Glyphosate in Soil and the Possibility of Leaching to Ground and Surface Waters: a Review. *Pest Manag. Sci.* 64 (4), 441–456. doi:10.1002/ps.1512

Bott, S., Tesfamariam, T., Kania, A., Eman, B., Aslan, N., Römheld, V., et al. (2011). Phytotoxicity of Glyphosate Soil Residues Re-mobilized by Phosphate Fertilization. *Plant and soil.* 342 (1), 249–263. doi:10.1007/s11104-010-0689-3

Bruand, A., Hartmann, C., and Lesturgez, G. (2005). "Physical Properties of Tropical sandy Soils: A Large Range of Behaviours," in Management Of Tropical Sandy Soils For Sustainable Agriculture. *A Holistic Approach for Sustainable Development of Problem Soils in the Tropics.*

Carlisle, S. M., and Trevors, J. T. (1988). Glyphosate in the Environment. *Water Air Soil Pollut.* 39 (3), 409–420.

Cederlund, H. (2017). Effects of spray Drift of Glyphosate on Nontarget Terrestrial Plants-A Critical Review. *Environ. Toxicol. Chem.* 36 (11), 2879–2886. doi:10.1002/etc.3925

Cheng, H. H. (1990). "Pesticides in the Soil Environment—An Overview," in *Pesticides in the Soil Environment: Processes, Impacts and Modeling, Volume 2,* 1–5.

Cornish, P. S., and Burgin, S. (2005). Residual Effects of Glyphosate Herbicide in Ecological Restoration. *Restor Ecol.* 13 (4), 695–702. doi:10.1111/j.1526-100x.2005.00088.x

Cuhra, M., Bøhn, T., and Cuhra, P. (2016). Glyphosate: Too Much of a Good Thing? *Front. Environ. Sci.* 4, 28. doi:10.3389/fenvs.2016.00028

De Jonge, H., De Jonge, L. W., Jacobsen, O. H., Yamaguchi, T., and Moldrup, P. (2001). Glyphosate Sorption in Soils of Different pH and Phosphorus Content. *Soil Sci.* 166 (4), 230–238. doi:10.1097/00010694-200104000-00002

Dick, R. E., and Quinn, J. P. (1995). Glyphosate-degrading Isolates from Environmental Samples: Occurrence and Pathways of Degradation. *Appl. Microbiol. Biotechnol.* 43 (3), 545–550. doi:10.1007/bf00218464

Ellis, J. M., and Griffin, J. L. (2002). Soybean (Glycine max) and Cotton (Gossypium Hirsutum) Response to Simulated Drift of Glyphosate and Glufosinate1. *Weed Tech.* 16 (3), 580–586. doi:10.1614/0890-037x(2002)016[0580:sgmacg]2.0.co;2

Gerritse, R., Beltran, J., and Hernandez, F. (1996). Adsorption of Atrazine, Simazine, and Glyphosate in Soils of the Gnangara Mound, Western Australia. *Soil Res.* 34 (4), 599–607. doi:10.1071/sr9960599

Ghafoor, A., Jarvis, N. J., Thierfelder, T., and Stenström, J. (2011). Measurements and Modeling of Pesticide Persistence in Soil at the Catchment Scale. *Sci. Total Environ.* 409 (10), 1900–1908. doi:10.1016/j.scitotenv.2011.01.049

Gimsing, A. L., Borggaard, O. K., and Bang, M. (2004a). Influence of Soil Composition on Adsorption of Glyphosate and Phosphate by Contrasting Danish Surface Soils. *Eur. J. Soil Sci.* 55 (1), 183–191. doi:10.1046/j.1365-2389.2003.00585.x

Gimsing, A. L., and Borggaard, O. K. (2002). Competitive Adsorption and Desorption of Glyphosate and Phosphate on clay Silicates and Oxides. *Clay miner.* 37 (3), 509–515. doi:10.1180/0009855023730049

Gimsing, A. L., and Borggaard, O. K. (2001). Effect of KCl and CaCl2 as Background Electrolytes on the Competitive Adsorption of Glyphosate and Phosphate on Goethite. *Clays. Clay Minerals.* 49 (3), 270–275. doi:10.1346/ccmn.2001.0490310

Gimsing, A. L., Borggaard, O. K., Jacobsen, O. S., Aamand, J., and Sørensen, J. (2004c). Chemical and Microbiological Soil Characteristics Controlling Glyphosate Mineralisation in Danish Surface Soils. *Appl. Soil Ecol.* 27 (3), 233–242. doi:10.1016/j.apsoil.2004.05.007

Gimsing, A. L., Borggaard, O. K., and Sestoft, P. (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 (6), 1718–1722. doi:10.1021/es030572u

Gorica, V., Vojislava, B., Miroslav, A., Tijana, Z., and Đurović-Pejčev, R. (2016). "Polar Pesticide Analyses: Validation of Glyphosate Determination in Soil by LC-MS/MS," in 22nd International Symposium on Analytical and Environmental Problems. Szeged, Hungary, 22.

Hanke, I., Wittmer, I., Bischofberger, S., Stamm, C., and Singer, H. (2010). Relevance of Urban Glyphosate Use for Surface Water Quality. *Chemosphere* 81 (3), 422–429. doi:10.1016/j.chemosphere.2010.06.067

Kanissery, R., Gairhe, B., Kadyampakeni, D., Batuman, O., and Alferez, F. (2019). Glyphosate: Its Environmental Persistence and Impact on Crop Health and Nutrition. *Plants* 8 (11), 499. doi:10.3390/plants8110499

Kanissery, R. G., Welsh, A., and Sims, G. K. (2015). Effect of Soil Aeration and Phosphate Addition on the Microbial Bioavailability of Carbon-14-Glyphosate. *J. Environ. Qual.* 44 (1), 137–144. doi:10.2134/jeq2014.08.0331

Kjaer, J., Olsen, P., Ullum, M., and Grant, R. (2005). Leaching of Glyphosate and Amino-Methylphosphonic Acid from Danish Agricultural Field Sites. *J. Environ. Qual.* 34 (2), 608–620. doi:10.2134/jeq2005.0608

Laitinen, P. (2009). Fate Of the Organophosphate Herbicide Glyphosate in Arable Soils and its Relationship to Soil Phosphorus Status. Doctoral Dissertation. MTT Agrifood Research Finland.

Laitinen, P., Siimes, K., Eronen, L., Rämö, S., Welling, L., Oinonen, S., et al. (2006). Fate of the Herbicides Glyphosate, Glufosinate-Ammonium, Phenmedipham, Ethofumesate and Metamitron in Two Finnish Arable Soils. *Pest Manag. Sci.* 62 (6), 473–491. doi:10.1002/ps.1186

Leiva, J. A., Nkedi-Kizza, P., Morgan, K. T., and Qureshi, J. A. (2015). Imidacloprid Sorption Kinetics, Equilibria, and Degradation in sandy Soils of Florida. *J. Agric. Food Chem.* 63 (20), 4915–4921. doi:10.1021/acs.jafc.5b00532

Lupi, L., Miglioranza, K. S. B., Aparicio, V. C., Marino, D., Bedmar, F., and Wunderlin, D. A. (2015). Occurrence of Glyphosate and AMPA in an Agricultural Watershed from the southeastern Region of Argentina. *Sci. total Environ.* 536, 687–694. doi:10.1016/j.scitotenv.2015.07.090

Mamy, L., Barriuso, E., and Gabrielle, B. (2005). Environmental Fate of Herbicides Trifluralin, Metazachlor, Metamitron and Sulcotrione Compared with that of Glyphosate, a Substitute Broad Spectrum Herbicide for Different Glyphosate-Resistant Crops. *Pest Manag. Sci.* 61 (9), 905–916. doi:10.1002/ps.1108

Mamy, L., Barriuso, E., and Gabrielle, B. (2016). Glyphosate Fate in Soils when Arriving in Plant Residues. *Chemosphere* 154, 425–433. doi:10.1016/j.chemosphere.2016.03.104

Neumann, G., Kohls, S., Landsberg, E., Stock-Oliveira Souza, K., Yamada, T., and Romheld, V. (2006). Relevance of Glyphosate Transfer to Non-target Plants via the Rhizosphere. *J.Plant Diseases and Protection.* ZEITSCHRIFT PFLANZENKRANKHEITEN PFLANZENSCHUTZ-SONDERHEFT- 20, 963.

Newton, M., Horner, L. M., Cowell, J. E., White, D. E., and Cole, E. C. (1994). Dissipation of Glyphosate and Aminomethylphosphonic Acid in North American Forests. *J. Agric. Food Chem.* 42 (8), 1795–1802. doi:10.1021/jf00044a043

Nomura, N. S., and Hilton, H. W. (1977). The Adsorption and Degradation of Glyphosate in Five Hawaiian Sugarcane Soils*. *Weed Res.* 17 (2), 113–121. doi:10.1111/j.1365-3180.1977.tb00454.x

Obreza, T. T., and Collins, M. E. (2008). *Common Soils Used for Citrus Production in Florida.* Gainesville, FL: EDIS, University of Florida, Cooperative Extension Service.

Obreza, T. T., and Morgan, K. T. (2008). *Nutrition of Florida Citrus Trees.* Gainesville, FL: EDIS, University of Florida, Cooperative Extension Service.

Okada, E., Costa, J. L., and Bedmar, F. (2019). Glyphosate Dissipation in Different Soils under No-Till and Conventional Tillage. *Pedosphere* 29 (6), 773–783. doi:10.1016/s1002-0160(17)60430-2

Piccolo, A., Celano, G., and Conte, P. (1996). Adsorption of Glyphosate by Humic Substances†. *J. Agric. Food Chem.* 44 (8), 2442–2446. doi:10.1021/jf950620x

Quinn, J. P., Peden, J. M. M., and Dick, R. E. (1988). Glyphosate Tolerance and Utilization by the Microflora of Soils Treated with the Herbicide. *Appl. Microbiol. Biotechnol.* 29 (5), 511–516. doi:10.1007/bf00269078

Salazar López, N. J., Silveira Gramont, M. I., Zuno Floriano, F. G., Rodríguez Olibarría, G., Hengel, M., and Aldana Madrid, M. L. (2016). Dissipation of Glyphosate from grapevine Soils in Sonora, Mexico. *Terra Latinoamericana* 34 (4), 385–391.

Sheals, J., Sjöberg, S., and Persson, P. (2002). Adsorption of Glyphosate on Goethite: Molecular Characterization of Surface Complexes. *Environ. Sci. Technol.* 36 (14), 3090–3095. doi:10.1021/es010295w

Shushkova, T., Ermakova, I., and Leontievsky, A. (2010). Glyphosate Bioavailability in Soil. *Biodegradation* 21 (3), 403–410. doi:10.1007/s10532-009-9310-y

Sørensen, S. R., Schultz, A., Jacobsen, O. S., and Aamand, J. (2006). Sorption, Desorption and Mineralisation of the Herbicides Glyphosate and MCPA in Samples from Two Danish Soil and Subsurface Profiles. *Environ. Pollut.* 141 (1), 184–194. doi:10.1016/j.envpol.2005.07.023

Sprankle, P., Meggitt, W. F., and Penner, D. (1975). Adsorption, Mobility, and Microbial Degradation of Glyphosate in the Soil. *Weed Sci.* 23, 229–234. doi:10.1017/s0043174500052929

Tong, M., Gao, W., Jiao, W., Zhou, J., Li, Y., He, L., et al. (2017). Uptake, Translocation, Metabolism, and Distribution of Glyphosate in Nontarget Tea Plant (Camellia Sinensis L.). *J. Agric. Food Chem.* 65 (35), 7638–7646. doi:10.1021/acs.jafc.7b02474

Torstensson, L. (1985). "Behavior of Glyphosate in Soils and its Degradation," in *Herbicide Glyphosate.* Editors E. Grossbard and D. Atkinson.

University of Florida (2020). *Florida Citrus Production Guide.* Gainesville, FL: EDIS, University of Florida, Cooperative Extension Service.

USDA (2018). *National Agricultural Statistics Service.* 2017 Fruit Chemical Use. Washington, DC: U.S.

USEPA (1995). *EPA Observational Economy Series, Vol 1: Composite Sampling.* EPA 230-R-95-005. Washington, DC: U.S. Government Printing Office.

USEPA (2008). *Fate, Transport and Transformation Test Guidelines* (OPPTS 835.1230 Adsorption/Desorption Batch Equilibrium). Washington, DC: US Government Printing Office.

Vereecken, H. (2005). Mobility and Leaching of Glyphosate: a Review. *Pest Manag. Sci.* 61 (12), 1139–1151. doi:10.1002/ps.1122

Wang, Y. J., Zhou, D. M., and Sun, R. J. (2005). Effects of Phosphate on the Adsorption of Glyphosate on Three Different Types of Chinese Soils. *J. Environ. Sci. (China)* 17 (5), 711–715.

Zhou, Y., Wang, Y., Hunkeler, D., Zwahlen, F., and Boillat, J. (2010). Differential Transport of Atrazine and Glyphosate in Undisturbed sandy Soil Column. *Soil Sediment. Contamination: Int. J.* 19 (3), 365–377. doi:10.1080/15320381003695272