

Title

Environmental fate of glyphosate in citrus production soils of Florida

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ABSTRACT: 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 ($K_{ads} = 14.28$ to 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, Herbicide half-life, Leaching.

INTRODUCTION

Glyphosate is considered a relatively environmentally safe herbicide because it is quickly inactivated in the soil by adsorption and degradation (Quinn et al., 1988). However, prior reports have 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 & Gimsing, 2008; Hanke et al., 2010). 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). Its non-judicious use in crop production has raised environmental and crop safety implications worldwide (Kanissery, 2019). The most significant among these is its persistence and movement in the soil and effects on non-target components of the crop ecosystem.

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., 2004). Glyphosate may also be transported to groundwater, surface water, and water-sediment by processes like surface runoff, erosion, drift, and leaching (Lupi et al., 2015; Newton et al., 1994; Ellis & Griffin, 2002; Shushkova et al., 2010). Major factors that affect glyphosate's persistence and movement in the soils are soil pH, soil type, mineralogy, texture, organic matter content, soil nutrient status, and surface vegetation cover (De Jonge, 2001; Laitinen et al., 2006; Mamy et al., 2016). Glyphosate-soil interaction occurs by processes such as adsorption (soil binding of herbicides) and desorption (the release of bound herbicide back into the soil solution), which plays an important role in predicting the availability; persistence and movement of the herbicide

in soil (Borggaard & Gimsing, 2008). Understanding such processes helps in utilizing glyphosate as a more effective, crop- and environmentally-safe weed management tool.

Florida's citrus-producing areas have soils with unique properties (e.g., 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 & Morgan, 2008; Obreza & Collins, 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 in Florida: southwest (Location: Immokalee; latitude: 26°28'7"N, longitude: 81°26'22"W), southeast (Location: Fort Pierce; latitude: 28°6'7"N, longitude: 81°41'35"W) and central (Location: Lake Alfred; latitude: 27°26'7"N, longitude: 80°25'25"W). Soils without a history of glyphosate application in the past two years were chosen in each sampling location. Soils were collected from five different sampling points in a transect fashion,

from the top layer (15 cm depth) from each location. 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).

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
Soil series	Spodosols	Alfisols	Entisols
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

Chemicals and reagents. The analytical standard (99.99% purity) of glyphosate in water (1000 mg L⁻¹) was procured from Restek (Bellefonte, PA, USA). Five different concentrations (5, 10, 25, 50, and 100 mg L⁻¹) of glyphosate were prepared in 0.1 molar potassium chloride (KCl) solution in water (Gimsing & 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 (data not presented). As suggested by the preliminary study, 4 g of air-dried soil were weighed and equilibrated with 20 mL of glyphosate in 0.1 molar KCl solution in 40 mL Teflon centrifuge tubes with threaded cap by shaking in a horizontal shaker (200 rpm) for 24 hours (Accinelli et al., 2005). 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. Following the equilibration, the soil suspension was centrifuged at 6000 rpm for 15 min. 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 (Table S1). The limit of detection for glyphosate in the analysis was

500 $\mu\text{g L}^{-1}$. 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. 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, 6000 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 hours 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 of glyphosate content in the soil samples was performed using HPLC-MS in a commercial laboratory (Waters Agricultural Laboratories, Camilla, GA). 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 (Fig. 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 (Fig. 1b,c), and each column was watered to field capacity and allowed to drain for 24 hr.

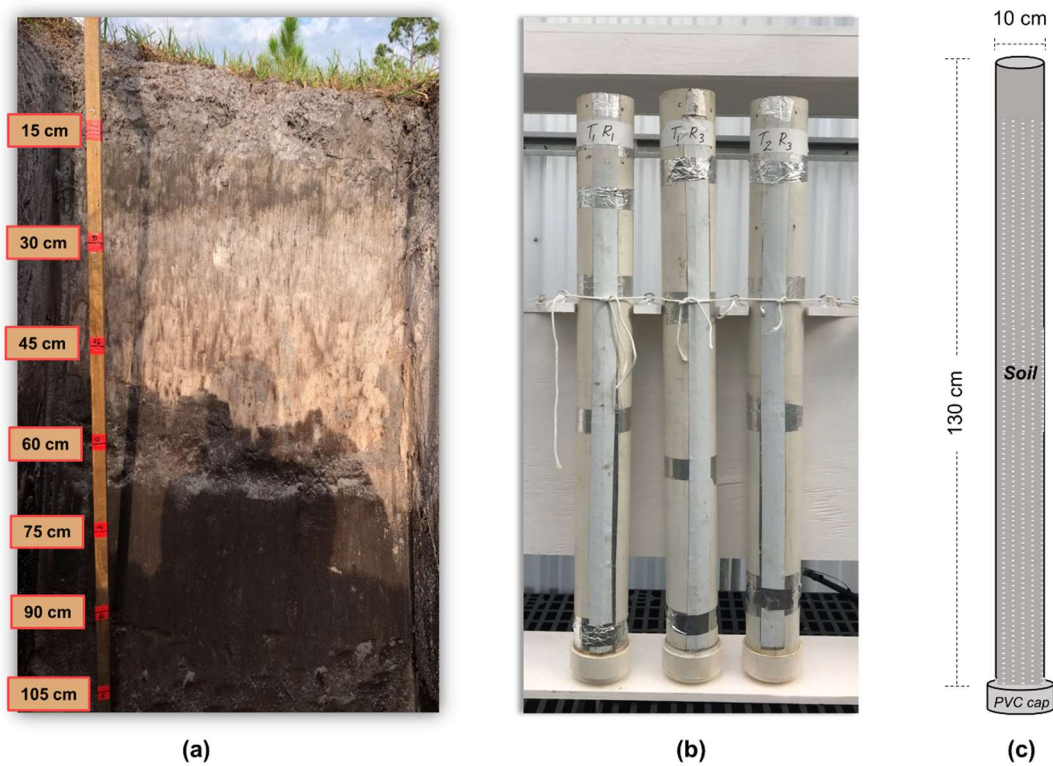


Figure 1: (a) Picture of soil profile used for packing the columns (b) Picture of soil leaching columns used in the experiment (c) Diagram of a soil leaching column.

Experimental design and treatments. The experiment was set up in a completely randomized design (CRD) with three replications. The treatments consisted of glyphosate application ($4.20 \text{ kg ae ha}^{-1}$) 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 CO₂ 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 in a commercial laboratory (Waters Agricultural Laboratories, Camilla, GA). The method detection limit for glyphosate and AMPA were 50 and 120 $\mu\text{g kg}^{-1}$ soil, respectively.

Data Analysis

The adsorption and desorption isotherms were fitted using the transformed Freundlich isotherm equation: $\log C_s = \log K_f + 1/n \log C_e$, 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.

The field dissipation data of glyphosate in soils were fitted into the first-order kinetics model $C_t = C_0 e^{-kt}$ where 'C₀' is the initial concentration ($\mu\text{g kg}^{-1}$ soil) of the herbicide in the soil, 'C_t' is the herbicide concentration ($\mu\text{g kg}^{-1}$ 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 $p \leq 0.05$.

RESULTS AND DISCUSSION

Adsorption-desorption study

For the range of herbicide concentrations (5 to 100 mg L⁻¹) and soils, adsorption data from the current experiment were well-fitted into the Freundlich isotherm model ($R^2 > 0.91$). Fig. 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 ($p \leq 0.05$) 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).

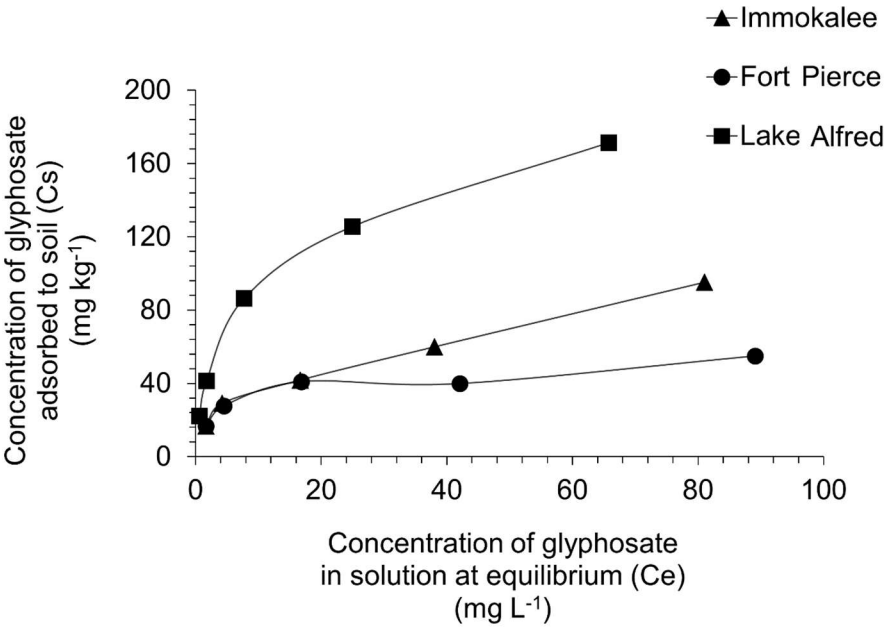


Figure 2. Freundlich adsorption isotherm plots of glyphosate in Florida’s citrus production soils

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Table 2. Adsorption (Freundlich model) parameters of glyphosate in Florida’s citrus production soils.

Soil / Location	K_{ads}^a	$1/n_{ads}^b$	R^{2c}
Immokalee	14.28 ^d (±0.83) B ^e	0.41 (±0.01)	0.98
Fort Pierce	16.56 (±0.17) B	0.27 (±0.01)	0.91
Lake Alfred	30.88 (±0.82) A	0.43 (±0.04)	0.98

^a K_{ads} Freundlich adsorption coefficient

^b $1/n_{ads}$ Adsorption isotherm slope

^c R^2 Goodness of fit for the Freundlich model

^d Mean ± 95% Confidence Interval

^e Letters beside the numeric values indicate Tukey’s HSD at $p \leq 0.05$. Values with the same letters are not significantly different

Desorption isotherms for glyphosate in all the soils also fitted into the Freundlich model ($R^2 > 0.84$) (Table 3). 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.

Table 3. Desorption (Freundlich model) parameters of glyphosate in Florida’s citrus production soils.

Soil / Location	K _{des} ^a	1/n _{des} ^b	R ^{2c}
Immokalee	13.30 ^d (±1.5) B ^c	0.42 (±0.06)	0.84
Fort Pierce	17.88 (±1.8) B	0.58 (±0.08)	0.84
Lake Alfred	38.51 (±1.4) A	0.70 (±0.02)	0.97

^a K_{des} Freundlich desorption coefficient

^b 1/n_{des} Desorption isotherm slope

^c R² Goodness of fit for the Freundlich model

^d Mean ± 95% Confidence Interval

^e Letters beside the numeric values indicate Tukey’s HSD at $p \leq 0.05$. Values with the same letters are not significantly different

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 10⁵ 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 &

Collins, 2008) and could be a plausible reason behind relatively lower adsorption and higher desorption of glyphosate in these soil types.

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). Clay minerals like iron (Fe) and aluminum (Al) oxides in the soil can provide binding or adsorption sites to the glyphosate (Gimsing & 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 & 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 & 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 (Sheals et al., 2002; Gimsing & Borggaard 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 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 3). 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 4. The dissipation of glyphosate from the surface soil (top 15 cm) over time (Fig. 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 day^{-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 (Fig. S1).

Table 4. 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 DT₅₀ Dissipation Half-life or 50% dissipation time

^b DT₉₀ 90% dissipation time

^c k Rate constant

^d R² Goodness of fit for simple first-order kinetic model

^e Mean ± 95% Confidence Interval

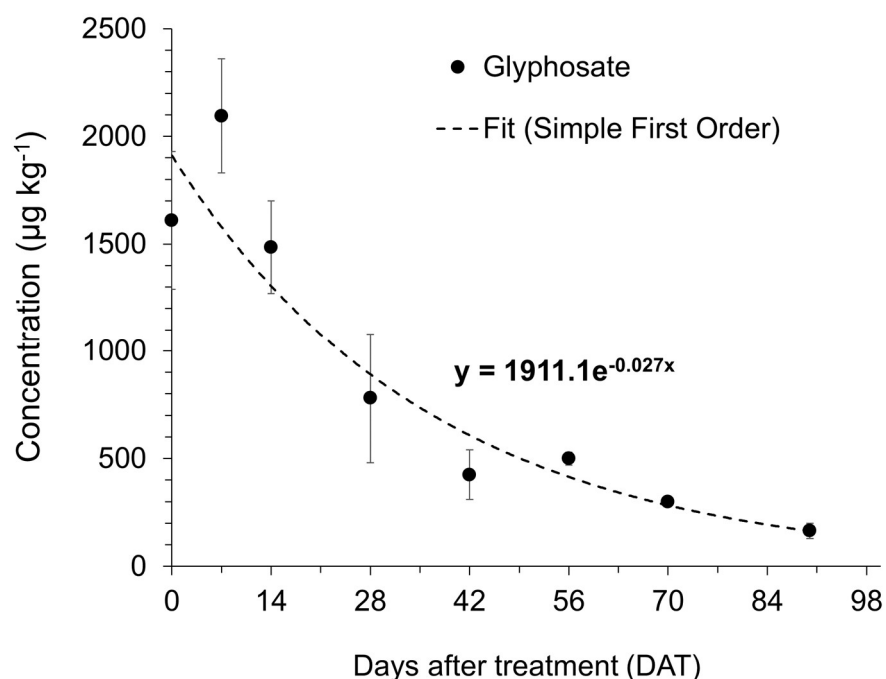


Figure 3. Field dissipation kinetics of glyphosate (4.20 kg ae ha⁻¹) in a citrus orchard

(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.

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 to 38 days. Glyphosate DT₅₀ 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 & Hilton 1977; Carlisle & 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; Bergstrom 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 López et al. (2016), where glyphosate concentrations reached a maximum in soil 10 to 18 days after application. 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 three months after the application, as noted from a prolonged DT_{90} . Researchers have reported a DT_{90} of over seven 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

Fig. 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.

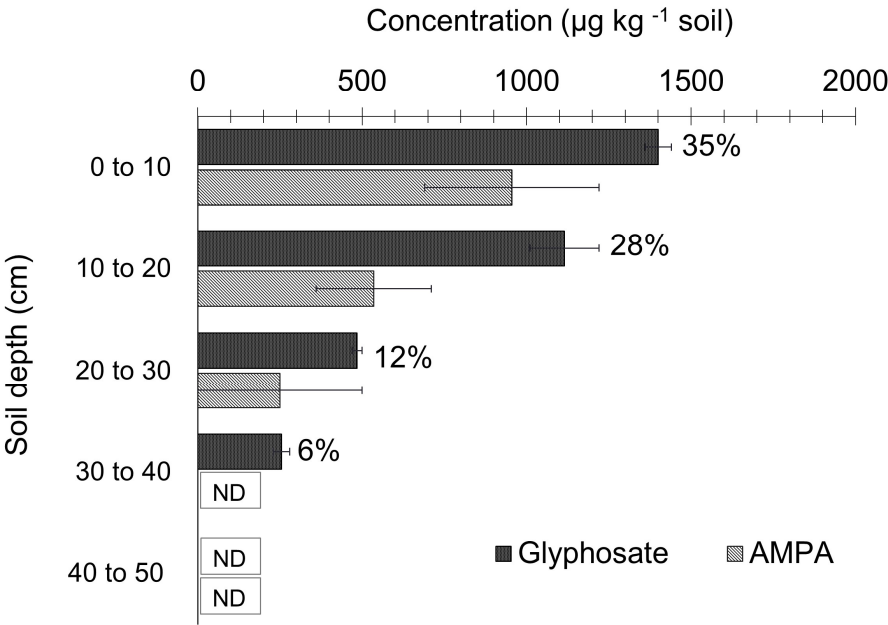


Figure 4. Vertical movement of glyphosate and AMPA in the soil leaching columns (40 Days after treatment - DAT). Error bars, wherever visible, indicate 95% Confidence Interval. Values near the glyphosate bars in the graph indicate glyphosate accumulation as the percentage of herbicide initially applied. 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.

Glyphosate has moved vertically up to 40 cm in the soil, as observed from soil columns. A similar trend was observed by Laitinen et al. (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 (Fig. 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 2000) that possibly restricted the downward movement of the herbicide (> 40 cm) into deeper soil layers. 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 2005; Tong et al., 2017).

CONCLUSIONS

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 F.L. 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.

SUPPLEMENTAL MATERIAL

The supplemental material contains additional detail on HPLC-MS conditions utilized during the analysis of glyphosate and information on the rainfall received during the field dissipation study (includes Table S1 and Fig. S1)

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430 **AUTHOR CONTRIBUTIONS**

431 Conceptualization, R.K. and B.G.; Methodology, B.G. and R.K.; Investigation, B.G.; Resources,
432 R.K.; Writing – Original Draft Preparation, B.G and R.K.; Writing – Review & Editing, W.L.,
433 P.D., D.K and O.B.; Supervision, R.K. P.D., D.K and O.B; Project Administration, R.K.;
434 Funding Acquisition, R.K.

435 **DATA AVAILABILITY**

436 The data presented in this study are available on request.

437 **CONFLICTS OF INTEREST**

438 The authors declared no conflicts of interest.

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SUPPLEMENTAL MATERIALS

Table S1. High-performance liquid chromatography-mass spectrometry (HPLC-MS) conditions used for the analysis of glyphosate in aqueous solution.

HPLC-MS conditions	Description/Value
Mobile phases:	
Mobile Phase A	50 mM Ammonium formate in Water (pH 2.9)
Mobile Phase B	Acetonitrile
Equilibration time	6 mins
Gradient:	
Mobile Phase A	100% (0-3 mins)
Mobile Phase B	0 to 100% (3-6 mins)
Column	Acclaim Trinity™ Q1, 3 x 100 mm
MS conditions:	
Ionization	-ve
Probe temperature	550 °C
Cone voltage	60 V
Glyphosate retention time	~2.69 mins

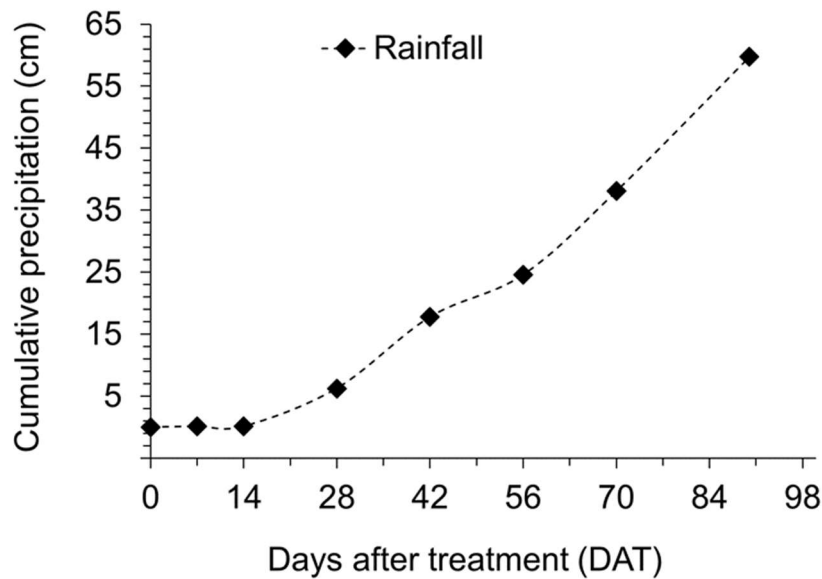


Figure S1. Cumulative rainfall received during the field dissipation experiment in citrus orchard. (Data obtained from FAWN, Immokalee, FL)

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