Adsorption, desorption and persistence of fomesafen in soil

Xiao Li,[a]* Timothy Grey,[b] Katilyn Price,[a] William Vencill[c] and Theodore Webster[d]

Abstract

BACKGROUND: Fomesafen provides control of glyphosate-resistant Palmer amaranth in cotton but frequent seedling injury has been reported. This study evaluated soil adsorption, desorption, and field persistence of fomesafen.

RESULTS: The Freundlich distribution coefficient (K_f) for fomesafen on seven US soils varied from 1.30 to 9.28 $\mu g^{1-1/n}\,g^{-1}\,mL^{1/n}$. The pesticide distribution coefficient (K_d) and soil organic carbon normalized adsorption coefficient (K_{OC}) varied from 1.11 to 12.76 mL g^{-1} and 58 to 1467 mL g^{-1}, respectively. The soils evaluated had desorption rates of 11.06% to 81.31% after a single desorption cycle. Soil pH, organic matter, sand, silt and clay content had a significant impact on fomesafen adsorption and desorption. Fomesafen field half-lives (DT_{50}) in Cecil sandy loam were 47 and 34 days, compared with 6 and 4 days in Tifton loamy sand when fomesafen was applied at 1× and 2× the label rate, respectively. The fomesafen dissipation rate decreased significantly under low-density polyethylene (LDPE) mulch compared with bare ground.

CONCLUSION: Fomesafen soil adsorption to soils was not strong and was affected by multiple soil properties. Fomesafen field persistence varied significantly between soil types and under ground cover. The data suggest that soils with a lower pH and higher clay content are less likely to produce crop injury due to greater fomesafen adsorption.
© 2018 Society of Chemical Industry

Keywords: fomesafen; adsorption; desorption; degradation, field dissipation

1 INTRODUCTION

Glyphosate-resistant and acetolactate synthase inhibitor-resistant Palmer amaranth (*Amaranthus palmeri* S. Wats.) in the southern USA has been consistently ranked as the most troublesome weed in multiple states and in multiple major row crops including cotton (*Gosspium hirsutum*), peanut (*Arachis hypogaea*) and soybean (*Glycine max*).[1] The expansion of herbicide-resistant Palmer amaranth has increased the use of soil residual herbicides for weed control in cotton production. These residual herbicides are considered crucial components of cotton weed control programs due to the lack of effective topical herbicide against resistant weeds.[2,3] Fomesafen is a residual herbicide that provides effective control of glyphosate-resistant and acetolactate synthase inhibitor-resistant Palmer amaranth in US cotton and soybean.[2,4,5] Fomesafen belongs to the diphenylether herbicide family; the mechanism of action of this family is inhibition of protoporphyrinogen oxidase (PPO), which causes failure in chlorophyll production and accumulation of radical oxygen species in plant cells.[6] Although in recent years, Palmer amaranth has evolved resistance to PPO inhibitor herbicides, a recent study showed that the resistant population was still responsive to several PPO inhibitor herbicides such as fomesafen flumioxazin, saflufenacil and sulfentrazone.[7] Fomesafen is registered in cotton and soybean at rates of 280 to 420 g ai ha^{-1} by Syngenta Crop Protection, Inc. (Greensboro, NC, USA).[8] Fomesafen can be applied pre-planting incorporated (PPI), pre-emergence (PRE) and post-directed in cotton, and it controls many troublesome broadleaf weeds including

pigweed (*Amaranthus* spp.), morning glory (*Ipomoea* spp.), jimsonweed (*Datura stramonium* L.), wild mustard (*Sinapis arvensis* L. ssp. *Arvensis*), black nightshade (*Solanum nigrum* L.) and ragweed (*Ambrosia* spp.).[8]

Fomesafen is a weak acid with a pK_a of 2.7. It has a solubility of 50 mg L^{-1} at pH 7 that decreases to < 1 mg L^{-1} at pH 1.[6] Guo et al.[9] tested the adsorption, desorption and mobility of fomesafen in six soils from China and noted that soil pH was more important than soil organic matter (OM) for adsorption; in addition, 44% to 81% of the adsorbed fomesafen was desorbed from these soils with one desorption process. Weber[10] reported that decreasing the suspension pH to 2 greatly increased adsorption of fomesafen by all sorbents studied (18% increase for H$^+$-saturated soil OM, 50% increase for Norfolk sandy loam, 53% increase for Ca^{2+}-saturated montmorillonite clay, 81% increase for Ca^{2+}-saturated soil OM, and 81% increase for Drummer silt loam). Fomesafen adsorption to Drummer silt loam and Norfolk sandy loam increased by 4.1- and

* Correspondence to: X Li, Department of Crop, Soil and Environmental Sciences, Auburn University, Auburn, AL 36849, USA E-mail: steveli@auburn.edu

a Department of Crop, Soil and Environmental Sciences, Auburn University, Auburn, AL, USA

b Department of Crop and Soil Sciences, University of Georgia, Tifton, GA, USA

c Department of Crop and Soil Sciences, University of Georgia, Athens, GA, USA

d Crop Protection Unit, USDA-ARS, Tifton, GA, USA

Table 1. Soil information of fomesafen adsorption and desorption study[a]

Location	Soil type	Taxonomy	pH	OM	Sand	Silt	Clay	CEC
						%		Meq/100 g
Athens, GA	Cecil sandy loam	Fine, kaolinitic, thermic Typic Kanhapludults	5.5	1.5	72	12	16	2.6
Plains, GA	Greenville sandy clay loam	Fine, kaolinitic, thermic Rhodic Kandiudults	5.6	2.7	60	10	30	7.1
Ty Ty, GA	Tifton loamy sand	Fine–loamy, kaolinitic, thermic Plinthic Kandiudults	5.6	1.0	90	6	4	2.5
Texas	Tremona sand	Loamy, fine sand, thermic Aquic Arenic Paleustalfs	7.9	0.4	92	2	6	4.2
Kentucky	Sonora silt loam	Fine–loamy, mixed, semiactive, mesic Typic Paleudalfs	6.9	3.5	38	46	16	14.0
Colorado	Haxtun sandy loam	Fine–loamy, mixed, superactive, mesic Pachic Argiustolls	8.0	1.4	60	26	14	26.0
Idaho	Minidoka silt loam	Coarse–silty, mixed, speractile, mesic Xeric Haplodorid	7.0	2.3	30	54	16	12.0

[a] Soil information was provided by University of Georgia Soil Testing Laboratory. Athens GA. CEC, cation exchange capacity

19-fold respectively when the natural soil pH (6.3 for Drummer silt loam and 5.3 for Norfolk sandy loam) was decreased to 2.[10] At agronomic soil pH ranges (5–8), fomesafen adsorption to Fe and Al oxides occur because many weak acids largely appear in their anionic forms.[11,12] Therefore, increased soil adsorption on acidic soil surfaces may reduce fomesafen mobility and bioavailability due to the formation of hydrophobic bonds between the fomesafen molecule and the lipophilic sites on the organic colloidal surfaces.[10,13]

Previous research indicated that the fomesafen soil half-life (DT_{50}) varies dramatically under different environmental and soil conditions. Rauch et al.[14] reported that fomesafen field DT_{50} was 28–66 days with an average of 50 days in a Madalin silty clay loam from New York. Mueller et al.[15] reported that the DT_{50} of fomesafen in a Sequatchie loam from Tennessee was 45.6 days. Fomesafen dissipation under anaerobic conditions was < 3 weeks and its field persistence varied significantly with DT_{50} from 180 to 360 days.[6] Because of its long soil persistence, fomesafen residue may injure susceptible crops such as corn (*Zea mays* L.), sugar beets (*Beta vulgaris* L.), sunflowers (*Helianthus annuus* L.) and sorghum (*Sorghum bicolor* L.) up to 1 year after application.[6,14,16]

Leaching could be another major dissipation pathway for fomesafen from the surface soil. Weber[17] suggested that fomesafen movement occurred in irrigated soils. Fomesafen exhibited greater mobility in Norfolk sandy loam compared with Cape Fear sandy loam, Drummer silt loam and Oxisol clay, when they were irrigated with 1.25 cm d^{-1} of water for 40 consecutive days (50 cm total). Liming this Norfolk sandy loam from pH 5.3 to 6.8 caused fomesafen to leach sooner and in greater initial amounts.[17] Fomesafen mobility was negatively related to soil OM, humic matter, pH and cation exchange capacity.[17] Fomesafen was reported to have greater mobility in a Red–Yellow Latosol from Brazil, which has a lower OM content and higher pH, than a Red–Yellow Argisol used in the same study that contained higher soil OM.[18] Although there is published research regarding fomesafen adsorption, desorption and soil mobility, limited data are available to indicate fomesafen soil adsorption and desorption, field persistence, and effect of different soil characteristics on fomesafen bioavailability to sensitive crops. In addition, fomesafen application in cotton production areas has increased significantly in the past several years because of the rapid expansion of herbicide-resistant Palmer amaranth. Total usage of fomesafen in all cotton-producing states increased by 6.5 times from 2007 to 2015.[19] In Georgia, 18 573 kg of fomesafen was applied on 66 636 ha in 2007 and this increased to 85 164 kg on 304 330 ha by 2015.[19] However, cotton growers in the southern USA have frequently observed seedling injury, stunting and stand reduction caused by fomesafen application and little analytical data are available to address this issue.[20–22] Fomesafen has recently received a 24C special local need label for Palmer amaranth control in several vegetables in Georgia, such as watermelon, tomatoes, squash and pepper. However, because of its relatively long soil persistence, fomesafen carryover injury on the subsequent sensitive crop planted in the same bed has also been reported by Georgia vegetable growers who utilize plasticulture in their production. Therefore, more data are needed to predict its soil adsorption and desorption, bioavailability, and persistence to prevent unacceptable crop injury. The objectives of this experiment were: (i) evaluate fomesafen soil adsorption and desorption as affected by various soil properties, (ii) evaluate fomesafen persistence under field conditions in two Georgia soils commonly found in cotton and vegetable production area, and (iii) evaluate fomesafen field persistence in uncovered soil versus in soil covered with low-density polyethylene (LDPE) mulch in vegetable production.

2 MATERIALS AND METHODS

2.1 Adsorption and desorption

Seven distinct soils sampled from depths of 0–15 cm in the field were used to evaluate fomesafen adsorption and desorption (Table 1). Three Georgia soils, and one each from Texas and Kentucky were included in the adsorption and desorption experiments because these soils represent the common soil types of major cotton growing regions in the southern USA where fomesafen is applied. Georgia soils typically have higher sand fractions and lower pH than other soils in this study. The Haxtun sandy loam from Colorado and Minidoka silt loam from Idaho were also chosen to evaluate fomesafen behavior in soils with high pH and low sand fraction. A commercial formulation of fomesafen sodium salt (Reflex® 2SL, Syngenta Crop Protection, Inc.) was used to prepare the CaCl$_2$ stock solutions. For the adsorption experiment, 10 g of air-dried and sieved soil (using a #10, 2 mm sieve) was added

to a 50-mL polypropylene centrifuge tube, and combined with 20 mL of 0.01 M $CaCl_2$ stock solution containing 1.3, 2.6, 5.2, 10.5 or 21 µg mL^{-1} of active ingredient of fomesafen. An adsorption kinetic experiment was conducted on Cecil sandy loam over a 24 h period using $CaCl_2$ stock solution containing 10.5 µg mL^{-1} of fomesafen to determine the time needed to reach adsorption equilibrium. The soil–herbicide mixture was shaken for 24 h at 22 °C to reach equilibrium and data indicated that equilibrium was reached after 24 h of shaking. The mixed slurry was then centrifuged at 4000 r.p.m. (Beckman Model TJ-6 centrifuge, Indianapolis, IN, USA) for 5 min, and 2 mL of supernatant was filtrated with 0.25 µm nylon syringe filter (Fisher Scientific, Pittsburgh, PA, USA) prior to HPLC analysis. The concentration difference between the initial and final equilibrium solutions was used to calculate fomesafen soil adsorption. Each soil/fomesafen concentration combination had three replications, and the adsorption experiment was repeated twice over time.

Soil samples treated with $CaCl_2$ stock solution containing 2.6, 10.5 and 21 µg mL^{-1} fomesafen for the adsorption study were used to perform a desorption study. The supernatant was centrifuged and decanted after initial equilibrium was reached, air-dried overnight, then 20 mL of blank $CaCl_2$ solution without fomesafen was added to each tube and shaken 24 h to achieve a new equilibrium, which later was quantified with HPLC to calculate fomesafen desorption rate from soil. Preparation procedures for desorption experiment were similar to the adsorption study and final liquid samples were analyzed by HPLC. The fomesafen desorption process was conducted once only on the selected soil samples. The experiment contained three replications and was repeated twice over time.

The adsorption data were modeled to the logarithmic form of the Freundlich isotherms:[13,23–25]

$$\log Cs = \log K_f + 1/n \log Ce \qquad (1)$$

where Cs (µg g^{-1}) is the amount of herbicide adsorbed at the equilibrium concentration Ce (µg mL^{-1}); $1/n$ is a constant that characterize the isotherm nonlinearity. K_f (µg$^{1-1/n}$ g^{-1} mL$^{1/n}$) is the Freundlich adsorption coefficient, an estimate of sorption capacity of each soil. K_{OC} (adsorption coefficient normalized to the soil organic carbon content, in mL g^{-1}) was calculated as:

$$K_{OC} = (K_d/OC\%) \times 100 \qquad (2)$$

where K_d (pesticide distribution coefficient between soil and soil solution, in mL g^{-1}) is calculated as:[26,27]

$$K_d = Cs/Ce \qquad (3)$$

K_d was calculated based on an equilibrium point of 1.3 µg mL^{-1} initial concentration of fomesafen.

OC% (organic carbon) was calculated based on laboratory soil OM analysis:

$$OC\% = OM\% \times 0.58 \qquad (4)$$

2.2 Fomesafen field dissipation

The first field experiment was conducted in 2013 to evaluate fomesafen persistence at Athens and Ty Ty, Georgia. Soil characteristics for these two soils can be found in Table 1. Neither field was treated with fomesafen in 2012 and no detectable fomesafen was found in these fields at the initiation of this experiment. In this experiment, cotton cultivar 'DP1137B2RF' (Deltapine®, Monsanto Co.,

St. Louis, MO, USA) was planted at both locations. Then, 280 and 560 g ai ha^{-1} of fomesafen (Reflex 2SL, Syngenta Crop Protection) were sprayed to field plots at Athens and Ty Ty, Georgia on 17 and 1 May 2013, respectively, immediately following cotton planting. Application was by backpack sprayer with four nozzle booms at 187 L ha^{-1} and sprayer calibration was performed before application. The plot size was 1.8×6.1 m. Conventional tillage was used for all locations in this experiment and there were no plant residues on the soil surface at application. The experiment was a completely randomized block design with four replications. Five soil samples were taken randomly from treated field plots of both locations using a soil sampler with a diameter of 10 cm and sampling depth of 0–7.5 cm; five samples were combined for each plot. Sampling timings were within 1 h after treatment, and then at 1, 2, 7, 14, 42, 56, 84, 98 and 126 days after application (DAT). After soil samples were taken, they were wrapped in aluminum foil immediately and kept frozen at −18 °C until extraction.

In the second field experiment, raised beds (80 cm wide, 20 cm tall) were formed at Ty Ty, Georgia and drip irrigation was installed on every bed. No fomesafen residue from previous applications was found in blank samples collected from these beds prior to application. Fomesafen of 280 g ai ha^{-1} (Reflex 2SL, Syngenta Crop Protection) was applied on the formed beds on 6 March 2009 and 4 March 2010 using backpack sprayers at 187 L ha^{-1}. A different part of this field was used to conduct this experiment to prevent cross-contamination from the previous year's experiment. Immediately after spraying, 32-µm thick LDPE mulch was installed on half of the sprayed bed with the other half left uncovered. Watermelon (*Citrullus lanatus*) was transplanted to covered and uncovered plots after LDPE mulch installation. The experiment was a completely randomized block design with four replications for both covered and uncovered treatments. Only one rate of fomesafen was applied in this experiment. Each treatment (or ground cover type) consisted of four plots (each 0.76 m wide by 12 m long). Four soil samples of 10 cm diameter from 0–8 cm depth were randomly collected by a plug sampler from each plot, and mixed into a single sample for that plot. Holes made on the LDPE mulch were covered with tape after sampling. Soil samples were taken 13 times in 2009 (1 h after treatment, and at 1, 5, 11, 18, 25, 31, 45, 59, 74, 88, 118 and 150 DAT), and 12 times in 2010 (1 h after treatment, and at 1, 5, 11, 18, 32, 46, 60, 75, 89, 119 and 151 DAT). They were stored at −18 °C in a freezer until extraction and detection using the methods described below. After HPLC analysis, the fomesafen concentration data for this experiment were converted to % of initial concentration at 1 h after application to better demonstrate dissipation of this herbicide in soil. Rainfall data were also collected at each experiment site by automated weather stations to assist data interpretation.

2.3 Sample extraction and fomesafen detection

Fomesafen soil samples were processed at the University of Georgia Athens campus. Field-collected samples were taken from the freezer, thawed for 4 h, and sieved using a 2-mm soil sieve. Soil moisture was measured for a batch of samples collected at the same location and the same timing by oven drying for 3 days at 50 °C. Different weights of moist soil were measured to achieve 50 g dry soil. Fomesafen residue was extracted by shaking the entire 50 g dry weight equivalent of the moist soil sample in each 250 mL round-bottom flask with 100 mL of 50 : 50 HPLC grade water and dichloromethane plus 0.5% acetic acid for 2 h. The soil/fomesafen slurry sample was then poured into three 50 mL polypropylene tubes and centrifuged at 4000 r.p.m. for 5 min.

The supernatant was transferred to a separation funnel, where the lower phase (dichloromethane) was collected in two 50-mL polypropylene centrifuge tubes. Dichloromethane in each centrifuge tube was evaporated to 25 mL, then combined and evaporated to dryness. Fomesafen residues was re-dissolved into 2 mL of 70 : 30 HPLC grade water and acetonitrile solution by sonication, then centrifuged at 14 500 r.p.m. for 2 min to remove impurities before HPLC detection. Fomesafen recovery efficiencies from Cecil sandy loam and Tifton loamy sand were 91% and 95% in the preliminary test when the initial fomesafen added in the soil was 1 ug g^{-1}. Fomesafen concentrations in each soil sample were corrected with recovery efficiency obtained from test extractions.

Fomesafen quantification was performed with Waters 2695 HPLC and Waters 2996 PDA detector. Separation was conducted by a Waters XTerra Shield RP18 column (4.6 × 250 mm, 5 µm; Waters Co. Milford, MA, USA) at 60 °C, using gradient mobile phases of 0.1% formic acid in water (A) and acetonitrile (B). The flow program ratio was set as 62% A/38% B initially, and linearly decreased to 10% A/ 90% B in 7.5 min, then held isocratic for 2 min. Fomesafen was eluted at 6.95 min without interference. The system flow rate was 0.75 mL min^{-1} and the detection wavelength was 290 nm. The fomesafen quantification limit in soil was 2 µg kg^{-1}. The quantification limit of fomesafen in water or water + acetonitrile solution was 0.05 ug mL^{-1}.

2.4 Statistical analysis

There was no significant effect of experiment repetition over time, therefore, adsorption and desorption data were combined over the repetitions for analysis. Log conversion was conducted in SAS (Version 9.3, SAS Institute Inc., Cary, NC, USA) and converted data were fitted into a linear regression model (logarithmic form of Freundlich isotherms) using PROC REG procedure, to calculate K_f and $1/n$ in the Freundlich isotherms. The PROC CORR procedure in SAS was used to conduct pairwise correlation to evaluate the effect of soil properties on fomesafen adsorption coefficient (K_f) and desorption. Pearson correlation coefficients and corresponding P-values are reported in Table 4. To describe fomesafen field dissipation data, non-linear regression was performed using Sigmaplot 12.0 (Systat Software, Inc., San Jose, CA, USA) and a single first-order kinetic function,

$$f(x) = b_0 e^{-b1(t)} \quad (5)$$

where the responsive variable is the fomesafen concentration in soil samples (in ppm or % of initial concentration at 1 h after treatment); b_0 is the model-estimated starting value of fomesafen concentration in soil when time t is 0; b_1 is the dissipation rate of fomesafen (slope) and t is the time elapsed after fomesafen was applied (days). Fomesafen DT$_{50}$ in field persistence experiments was calculated as:

$$DT_{50} = -\ln(0.5)/b_1 \quad (6)$$

3 RESULTS

3.1 Fomesafen adsorption kinetics

Fomesafen adsorption was biphasic in nature, with 66% fomesafen in the solution rapidly adsorbed to Cecil sandy loam at 30 min when the starting fomesafen concentration in the solution was 10.5 µg mL^{-1} (Fig. 1). Adsorption increased to 72% at 1 h, and then slowly increased to 76% after 8 h of continuous shaking. This was consistent with Guo et al.[9] who reported that fomesafen
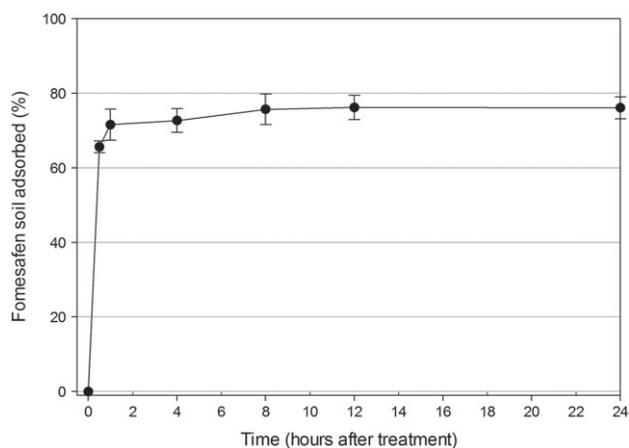

Figure 1. Fomesafen adsorption to Cecil sandy loam over a 24 h period compared with total amount applied. Error bars represent standard error of each mean (SEM). The initial fomesafen concentration in the mixing solution was 10.5 µg mL^{-1}.

adsorption and desorption could reach equilibrium after shaking for 1 h. Exposing additional sorption sites on soil particles as a result of prolonged shaking could have caused the slow increase of herbicide sorption after the initial rapid phase.[28–30]

3.2 Adsorption and desorption

Fomesafen sorption on seven soils evaluated in this study is shown in Fig. 2. Adsorption non-linearity occurred in this experiment because the value of $1/n$ ranged from 0.54 to 0.99 (Table 2). The Freundlich adsorption isotherms equation provided a good description of data with $r^2 \geq 0.97$ for all seven soils. Fomesafen adsorption was generally low for soils used in this study. The highest K_f was recorded with Cecil sandy loam (9.28 mL g^{-1}) and lowest with Tremona sand (1.30 mL g^{-1}). Most of the soils examined (except for Cecil sandy loam and Greenville sandy clay loam) had K_d values < 10 mL g^{-1} at an initial fomesafen concentration of 1.3 µg mL^{-1}, which indicates that fomesafen is not tightly bound to the surface in these soils and soil movement may be possible under some environmental conditions. The K_{OC} of fomesafen varied from 58 to 1467 mL g^{-1} on the soils studied in this experiment. Typically, a hydrophobic molecule has a greater possibility of leaving the aqueous phase and forming strong hydrophobic bonds with OM in soil. If this process is relatively independent of other soil factors, then the K_{OC} of this molecule will be relatively constant across a range of soils.[31] This was observed with flumioxazin soil adsorption,[30] in which OM had a significant impact on flumioxazin adsorption and the K_{OC} of flumioxazin only varied 1.6-fold over six soils (from 116 to 200 mL g^{-1}) because flumioxazin has low water solubility (1.78 mg L^{-1}) and is not ionizable.[32] However, this is not the case for fomesafen because it is a weak acid (pK_a of 2.7) with moderate water solubility (50 mg L^{-1}), and its K_{OC} varied 25.3-fold in this study (from 58 to 1467 mL g^{-1}). These results suggest that OM is not be the major adsorptive fraction in the soil matrix and other soil properties (pH, sand, silt clay content, iron and aluminum oxide, etc.) might influence fomesafen adsorption.

Fomesafen desorption from the soils examined in this study varied between 10% and 81% following a 24 h desorption process (Table 3). Fomesafen in the Cecil sandy loam, Greenville sandy clay loam, Sonora silt loam and Minidoka silt loam showed lower desorption rates than in the other soils studied, with only 11.06–29.11% of the adsorbed fomesafen being desorbed.
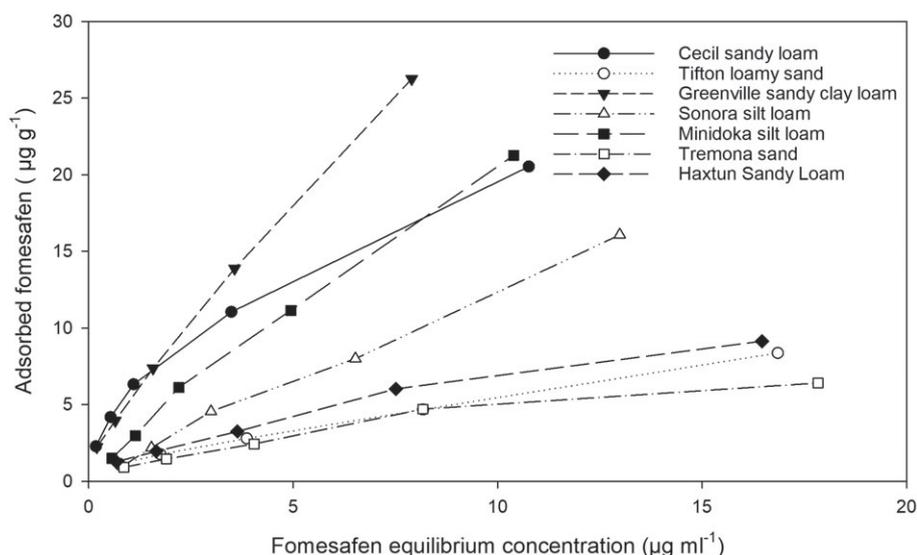
Figure 2. Fomesafen adsorption to seven US soils.

Table 2. Coefficient estimates for fomesafen sorption to various soils

Soil type	K_f ($\pm$SEM)[a]	K_d (mL g^{-1})[b]	K_{OC} (mL g^{-1})	$1/n$ ($\pm$SEM)	r^2
Cecil sandy loam	9.28 ± 0.68	12.76	1467	0.54 ± 0.02	0.97
Greenville sandy clay loam	7.76 ± 0.45	11.84	756	0.67 ± 0.02	0.99
Tifton loamy sand	1.70 ± 0.15	1.46	252	0.64 ± 0.02	0.98
Tremona sand	1.30 ± 0.12	1.11	478	0.67 ± 0.02	0.98
Sonora silt loam	1.35 ± 0.13	1.18	58	0.99 ± 0.02	0.98
Haxtun sandy loam	2.05 ± 0.15	1.89	233	0.64 ± 0.02	0.98
Minidoka silt loam	2.87 ± 0.17	2.56	192	0.91 ± 0.01	0.99

[a] SEM, standard error of the mean. Unit for K_f is µg$^{1-1/n}$ g^{-1} mL$^{1/n}$.
[b] K_d was calculated using the equilibrium concentration of each soil type when initial fomesafen concentration in CaCl$_2$ solution was 1.3 µg mL^{-1}.

The highest fomesafen desorption values were recorded for Tremona sand, Tifton loamy sand and Haxtun sandy loam, and 25.80–81.31% of the adsorbed fomesafen was desorbed from these soil types. Fomesafen was more readily desorbed from the soil surface at a higher initial concentration than a lower concentration. Similar findings have been reported by Morillo et al.[31] on norflurazon desorption from 17 European soils and by Pusino et al.[12] on imazapyr desorption from six Italian soils; these two herbicides also demonstrated a high desorption rate at high initial concentrations.

Pairwise correlation (Table 4) results suggested that soil pH and clay content played a significant role during adsorption. Pearson's correlation coefficient for pH and clay to K_f was −0.6832 and 0.6444, with corresponding *P*-values of 0.0006 and 0.0016. This indicated that pH and clay were more important than other soil properties for fomesafen adsorption. Previous studies have confirmed that soil pH was more important than OM during fomesafen soil adsorption.[9] Low pH decreases fomesafen water solubility and increases its affinity to soil OM due to the formation of hydrophobic bonds between the fomesafen molecule and lipophilic sites on the organic colloidal surfaces.[13] Therefore, pH was inversely correlated with fomesafen adsorption in this study (Table 4). For desorption, all soil parameter listed in Table 4 were significant except for cation exchange capacity. OM (−0.6306) and sand fraction (0.5812) had the greatest impact on fomesafen desorption,

Table 3. Percentage of fomesafen desorbed from soil following one 24 h desorption process

	Fomesafen desorption rate ($\pm$SEM)[a]		
		10.5 µg mL^{-1}	
Soil type	2.6 µg mL^{-1}	%	21 µg mL^{-1}
Cecil sandy loam	11.06 ± 1.72	18.73 ± 3.97	29.11 ± 5.24
Greenville sandy clay loam	28.28 ± 3.47	20.58 ± 3.82	24.08 ± 1.47
Tifton loamy sand	25.80 ± 5.01	45.96 ± 6.66	49.29 ± 8.87
Tremona sand	41.89 ± 2.91	48.43 ± 2.77	81.31 ± 4.2
Sonora silt loam	16.54 ± 1.89	16.21 ± 2.21	22.86 ± 2.94
Haxtun sandy loam	39.98 ± 3.21	48.08 ± 2.94	70.27 ± 3.37
Minidoka silt loam	9.92 ± 1.48	11.82 ± 1.47	16.54 ± 1.76

[a] Means presented in the table represent the percentage of fomesafen desorbed with one 24 h desorption process compared with total amount of fomesafen adsorbed to each soil type after reaching equilibrium. Three fomesafen concentrations were used to initiate the adsorption process. SEM, standard error of the mean.

followed by pH (0.4922), silt (−0.4883) and clay (−0.4502). Sand fraction and soil pH were positively related to desorption, whereas while silt, clay and OM were negatively related to desorption,

Table 4. Pairwise correlations of soil parameters to fomesafen soil adsorption (K_f) and desorption rate shown in Tables 2 and 3[a]

Parameters	Adsorption (K_f)		Desorption rate	
	correlation	P-value	Correlation	P-value
Sand	0.0101	0.9655	0.5812	**0.0057**
Silt	−0.2789	0.2209	−0.4883	**0.0247**
Clay	0.6444	**0.0016**	−0.4502	**0.0406**
pH	−0.6832	**0.0006**	0.4922	**0.0234**
CEC	−0.3648	0.1039	0.1664	0.4710
OM	0.1538	0.5056	−0.6306	**0.0022**

[a] PROC CORR procedure in SAS was used to conduct pairwise correlation in order to evaluate the effect of soil properties on fomesafen adsorption coefficient (K_f) and desorption rate. P-values bold indicate significant correlation at $P = 0.05$. Desorption rates were calculated using 2.6, 10.5, and 21 $\mu g\ mL^{-1}$ initial fomesafen concentration. CEC, cation exchange capacity.

which indicates fomesafen leaching potential and bioavailability may be increased in alkaline soils with a high sand fraction and low OM content. Higher fomesafen mobility has been reported in a Norfolk sandy loam compared with other soils with higher OM and a lower sand fraction.[17] Moreover, liming this Norfolk soil increased fomesafen mobility.

3.3 Fomesafen field dissipation

The first field dissipation experiment revealed significant differences among fomesafen dissipation rates in Cecil sandy loam and Tifton loamy sand (Fig. 3). The DT_{50} values for the 280 and 560 g ai ha^{-1} treatment were 47 and 34 days respectively for Cecil sandy loam. In Tifton loamy sand, DT_{50} values were 6 and 4 days, respectively, for the 280 and 560 g ai ha^{-1} treatments (Table 5). Fomesafen residues from the 280 and 560 g ai ha^{-1} treatments were detectable up to 126 DAT in Cecil sandy loam but were not found in Tifton loamy sand by 28 DAT. Least significant difference analysis indicated that the dissipation rate (b_1) varied significantly between soils and rates (Table 5). Cumulative rainfall from 0 to 7, 0 to 30 and 0 to 126 DAT at Athens (Cecil sandy loam) and Ty Ty (Tifton loamy sand) field trial sites were 88.4 and 31.0, 104.6 and 75.2, and 753.8 and 717.3 mm, respectively. Both locations received their first rainfall within 72 h after application, whereas the Athens trial received 2.85 times more precipitation within the first 7 DAT. The average maximal daily temperature during 0–30 DAT at the Athens and Ty Ty field trials was 24.9 and 27.2 °C, respectively. Therefore, quicker dissipation rates in Tifton loamy sand were not likely due to differences in rainfall or temperature between these two locations. Dissipation of herbicide in soil and on plants was dependent on the physicochemical properties of the herbicide and environmental conditions.[33] Differences in soil dissipation have been reported for diphenylether herbicides such as fomesafen. Fomesafen DT_{50} varied from 180 to 360 days under field conditions[8] and the DT_{50} of three diphenylether herbicides (chlornitrofen, nitrofen and chlomethoxynil) varied from 9 to 173, 3 to 87 and 8 to 64 days, respectively, in six Japanese soils.[34] Low K_d and K_f, and a higher desorption rate in Tifton loamy sand, compared with Cecil sandy loam, may have resulted in the dissipation differences between these two soils.

In the second field dissipation experiment, the fomesafen dissipation rate was significantly slower under LDPE mulch than in bare ground for in both 2009 and 2010 studies (Table 6, Fig. 4). DT_{50} of
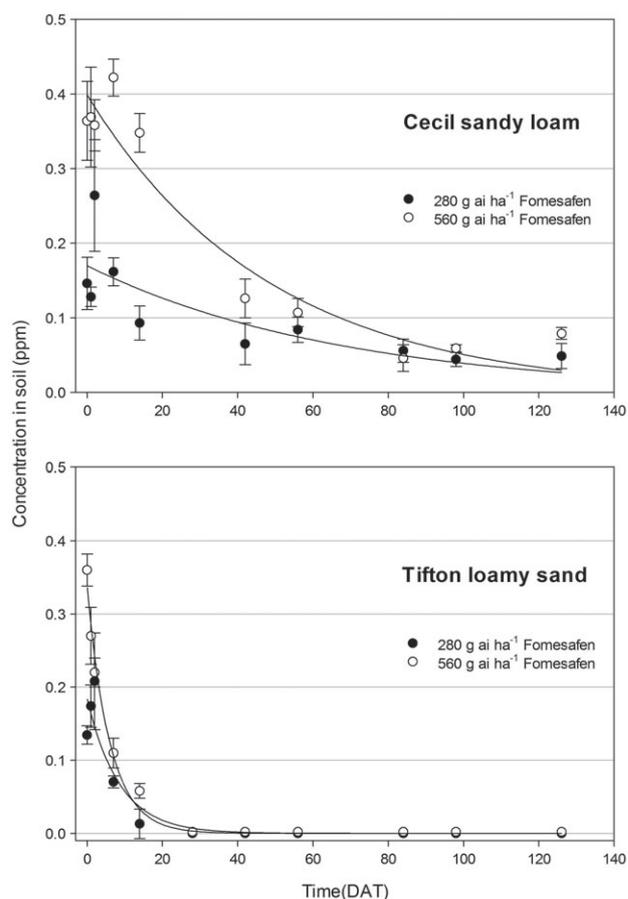

Figure 3. Fomesafen persistence in Cecil sandy loam and Tifton loamy sand. Error bars represent standard error of each mean (SEM). Data described by single first-order kinetic model and parameter estimates are listed in Table 5.

fomesafen under LDPE mulch was 46 and 38 days for 2009 and 2010 experiments, respectively, compared with 2 and 12 days in bare ground for the same two years. Fomesafen dissipation rate (b_1) in 2009 and 2010 did not differ significantly under LDPE mulch and dissipation pattern is very similar between these two years. However, dissipation in bare ground in 2009 was faster than in 2010 (Table 6). The total rainfall during 2009 and 2010 the field experiments was 780 and 520 mm, respectively. However, accumulated rainfall during the first 30 days of the experiment was 429 mm in 2009, compared with 51 mm in the first 30 days in 2010. Greater rainfall in the first 30 days of the 2009 experiment may explain the quicker fomesafen dissipation observed in bare ground plots, which indicated that leaching might be an important dissipation pathway for fomesafen in that year. Fomesafen has been found to have noticeable leaching potential by previous research. Costa et al.[18] reported moderate mobility of fomesafen in three soils up to a depth of 15–20 cm in leaching columns. Fomesafen leaching was affected mainly by soil types, OM and soil pH in their study.[18] As indicated by the results of fomesafen laboratory incubation experiment from Porter et al.,[35] fomesafen is relative persistent to microbial degradation with a DT_{50} of ∼ 100 days in Tifton loamy sand. Considering that fomesafen is not readily degraded in this soil and LDPE mulch prevents water penetration directly during rainfall, it is reasonable to speculate that faster dissipation rates in bare ground plots were mainly caused by leaching

Table 5. Parameter estimates of fomesafen persistence in surface soil under field conditions[a]

Soil type	Rate (g ai ha⁻¹)	$b_0 \pm$ SEM (µg g⁻¹)	$b_1 \pm$ SEM[b]	DT$_{50}$ (day)[c]	*F*-value	*P*-value	r^2
Cecil sandy loam	280	0.1699 ± 0.0222	0.0147 ± 0.0055 d	47	13.82	0.0059	0.6334
	560	0.3987 ± 0.0234	0.0206 ± 0.0035 c	34	101.68	<0.0001	0.9271
Tifton loamy sand	280	0.1829 ± 0.0215	0.1136 ± 0.0414 b	6	60.67	<0.0001	0.8835
	560	0.3358 ± 0.0120	0.1651 ± 0.0177 a	4	667.16	<0.0001	0.9882

[a] Single first-order kinetic model $f(x) = b_0 e^{-b1(x)}$ was used for regression. SEM, standard error of the mean. Soil samples were taken from a depth of 0–7.5 cm.
[b] Means followed by the same letter are not significant at 0.05 level using LSD separation.
[c] DT$_{50}$, days required for 50% herbicide dissipation.

Table 6. Parameter estimates of fomesafen soil persistence in surface soil under low-density polyethylene (LDPE) mulch and in bare ground[a]

Cover type	Year	$b_0 \pm$ SEM (%)	$b_1 \pm$ SEM[b]	DT$_{50}$ (day)[c]	F value	P value	r^2
LDPE mulch	2009	93.61 ± 7.09	0.0152 ± 0.0029 c	46	60.47	<0.0001	0.8461
	2010	102.04 ± 7.39	0.0183 ± 0.0032 c	38	74.82	<0.0001	0.8718
Bare ground	2009	97.72 ± 3.42	0.4633 ± 0.0518 a	2	819.56	<0.0001	0.9868
	2010	82.82 ± 7.99	0.0599 ± 0.0133 b	12	74.79	<0.0001	0.8718

[a] Single first-order kinetic model $f(x) = b_0 e^{-b1(x)}$ was used for regression. SEM, standard error of the mean.
[b] Means followed by the same letter are not significant at 0.05 level using LSD separation.
[c] DT$_{50}$, days required for 50% herbicide dissipation.

and the physical movement of fomesafen deeper into the soil profile beyond sampling depth, rather than microbial degradation.

4 DISCUSSION

Fomesafen may possess greater mobility and bioavailability to crops if applied to soils with a high sand fraction, high pH and low OM, as indicated by the results of this study. In this scenario, the fomesafen concentration in soil solution is high because of less adsorption. Bioavailable fomesafen in soil solution can be readily taken up by cotton seeds during germination and cause seedling injury. This injury problem could be worse if seeds are planted too deep in the soil, which allows longer exposure of the cotyledon and hypocotyl to fomesafen residues in soil solution.[36] Growers need to be cautious about potential crop injury in soils that show weak adsorption to fomesafen, especially when fomesafen is applied PRE at high rates or in combination with other residual herbicides. Low seed vigor, deep planting, and heavy rainfall after planting, but before seedling emergence may aggravate this problem. Cotton bioassay grown in the same experiments from which soil samples were taken to study fomesafen field persistence indicated that cotton exhibited greater sensitivity to fomesafen in Tifton loamy sand than in Cecil sandy loam.[37] Fomesafen application at 1120 and 2240 g ai ha⁻¹ reduced cotton seedling height by 17% and 41% respectively compared with non-treated check in Tifton loamy sand. A fomesafen application rate of 2240 g ai ha⁻¹ reduced cotton yield by 29% in Tifton loamy sand, but no height or yield reduction was observed with any rate of fomesafen applied to Cecil sandy loam in that study.[37] These field observations could be explained by weaker fomesafen adsorption to Tifton loamy sand than Cecil sandy loam found in this study. Previous research also indicated that cotton exhibited most injury when fomesafen was applied PRE, while PPI application and strip-tillage after application could effectively reduce the injury of fomesafen and other PPO inhibitors to cotton.[2,38] These findings indicated

that mechanical incorporation may have reduced herbicide concentrations in surface soil and reduced potential injury to cotton seedlings.

Microbial degradation may have a significant role in fomesafen dissipation.[39,40] Porter et al.[35] have reported DT$_{50}$ of fomesafen varied from 80 to 128 days in Tifton loamy sand when the treated surface soil was incubated under aerobic conditions in laboratory incubator. The mean DT$_{50}$ was 100 ± 20 days in that study, which was considered moderately persistent. Some bacterial strains capable of degrading fomesafen and other diphenyl ethers have been isolated from soil and have shown promise to degrade fomesafen in culture medium.[39,40] Costa et al.[18] reported that fomesafen DT$_{50}$ values in conventional tilled and no-till fields were 99 and 114 days, and 60 and 71 days, respectively. Considering that fomesafen is fairly tolerant to microbial degradation and moderately persistent in the field, the differences in fomesafen field dissipation between two Georgia locations in this study may be mostly explained by different levels of fomesafen retention to these two soil types (K_f), rather than by other factors such as biological degradation, temperature and rainfall.

Previous studies have confirmed that halosulfuron and *S*-metolachlor dissipation was more rapid in bare soil than in soil under LDPE mulch.[41] The dissipation of linuron, pendimethalin, chorobromuron and flurochloridone was decreased when applied to soil under perforated polyethylene tarp compared with in bare ground.[42] In this study, the fomesafen dissipation rate was significantly reduced in soil under LDPE mulch compared with the bare ground scenario in both years of the study because LDPE mulch may reduce or prevent photolysis, volatility loss, leaching and surface run-off of pesticides, and considering that fomesafen was not very susceptible to biological degradation in this soil.[35] Greater fomesafen dissipation rate in bare ground plots in the 2009 experiment compared with LDPE mulch-covered plots in that experiment suggested that leaching caused by rainfall may play a significant role in fomesafen field dissipation. Because of
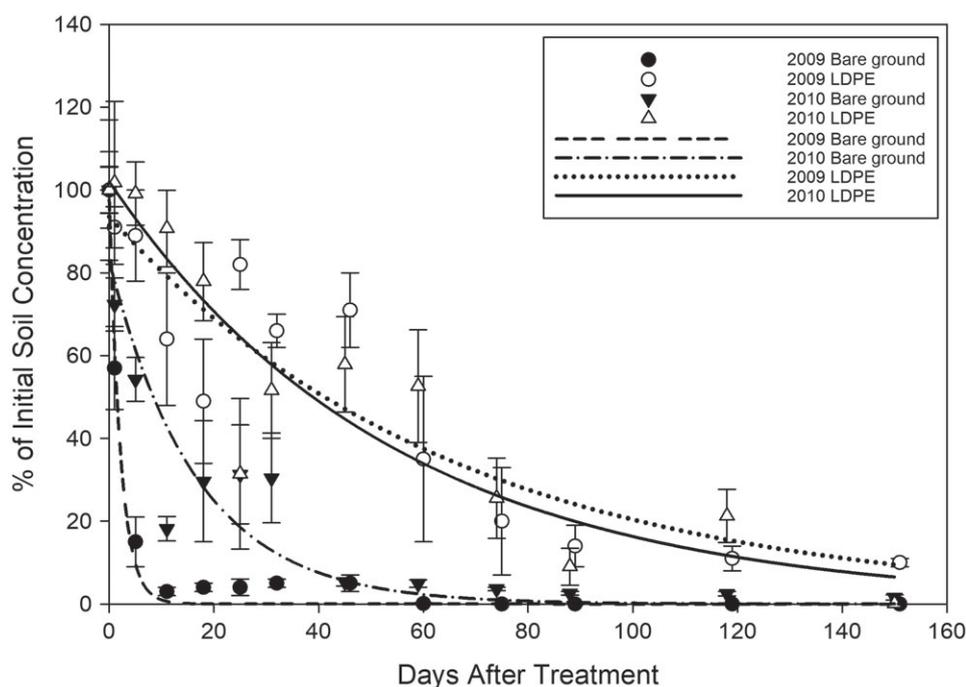
Figure 4. Fomesafen persistence in Tifton loamy sand under low-density polyethylene (LDPE) tarp and bare ground in 2009 and 2010. Error bars represent standard error of each mean (SEM). Data described by single first-order kinetic model and parameter estimates are listed in Table 6.

the limitations of the sampling method and depth in this study, this assumption cannot be directly verified. Further investigation is needed to evaluate field leaching potential of fomesafen in US cotton-growing areas and correlate those data to surface persistence to elucidate fomesafen dissipation from soil surface. In vegetable production in the southern USA where LDPE mulch is widely used, growers typically use the same LDPE mulch on raised beds for three or four vegetable crops before removing them to save production costs. Fomesafen applied to a raised bed and covered by LDPE may persist beyond one crop and potentially injure sensitive crops planted later due to a lack of leaching and relatively slow microbial degradation. The results from this study may provide insight into this complex problem and help growers make better management decisions in future. Based on the results of this study, it is reasonable to speculate that long fomesafen persistence and the greater possibility of carryover injury to sensitive crops planted in the same year (e.g., fall vegetables) may occur in soils with lower pH and higher soil clay content, particularly when environmental conditions are unfavorable for microbial degradation.

5 CONCLUSION

Fomesafen adsorption and desorption were affected by multiple soil characteristics such as pH, OM, sand, silt and clay content. Fomesafen persistence in surface soil was significantly longer in Cecil sandy loam compared with Tifton loam sand, possibly due to the 5.46 times higher K_f of Cecil sandy loam. Fomesafen field persistence was increased under LDPE mulch compared with in bare soil, which indicates that leaching in this study might be a major dissipation pathway because LDPE mulch inhibits photolysis, volatilization and surface run-off. Fomesafen injury to a sensitive crop may be increased in soils with lower pH and higher clay content.

REFERENCES
1 Webster TM, *Weed Survey Southern States, Broadleaf Crop Subsection*. [Online]. Southern Weed Science Society. Westminster, CO. (2013). Available: http://www.swss.ws/wp-content/uploads/2013/09/Southern-Weed-Survey-2013-Tables-BL-Crops.pdf [22 February 2018].
2 Culpepper AS, *Impact of EPA's Ecological Risk Assessment for Fomesafen*. (2009). [Online]. Subject: re-registration of fomesafen. Available: https://www.regulations.gov/searchResults?rpp=25&po=0&s=EPA-HQ-OPP-2006-0239&fp=true&ns=true [20 April 2018].
3 Sosnoskie LM, Kichler JM, Wallace RD and Culpepper AS, Multiple resistance in Palmer amaranth to glyphosate and pyrithiobac confirmed in Georgia. *Weed Sci* **59**:321–325 (2011).
4 Bond JA, Oliver LR and Stephenson DO IV, Response of Palmer Amaranth (*Amaranthus palmeri*) accessions to glyphosate, fomesafen and pyrithiobac. *Weed Technol* **20**:885–892 (2006).
5 Gardner AP, York AC, Jordan DL and Monks DW, Management of annual grasses and *Amaranthus* spp. in glufosinate-resistant cotton. *J Cotton Sci* **10**:328–338 (2006).
6 Anonymous, Fomesafen, in *Herbicide Handbook*, 9th edn, ed. by Senseman SA. Weed Science Society of America, Lawrence, KS, pp. 207–208 (2007).
7 Umphres A, Steckel L and Mueller T, Control of protoporphyrinogen oxidase inhibiting herbicide resistant and susceptible Palmer amaranth (*Amaranthus palmeri*) with soil-applied protoporphyrinogen oxidase-inhibiting herbicides. *Weed Technol* **32**:95–100 (2018).
8 Anonymous, *Reflex Section 3 Label*. (2016). [Online]. Available: http://www.syngenta-us.com/current-label/reflex [21 August 2018].
9 Guo J, Zhu G, Shi J and Sun J, Adsorption, desorption and mobility of fomesafen in Chinese soils. *Water Air Soil Pollut* **148**:77–85 (2003).
10 Weber JB, Ionization and sorption of fomesafen and atrazine by soils and soil constituents. *Pestic Sci* **39**:31–38 (1993).
11 Newby SE and White BG, PP021: leaching on soil thick-layer chromatograms. Report RJ0156B. ICI, London, p. 4 (1981).

12 Pusino A, Petretto S and Gessa C, Adsorption and desorption of Imazapyr by soil. *J Agric Food Chem* **45**:1012–1016 (1997).

13 Tanford C, *The Hydrophobic Effect*. Wiley, New York (1973).

14 Rauch BJ, Bellinder RR, Brainard DC, Lane M and Thies JE, Dissipation of fomesafen in New York state soil and potential to cause carryover injury to sweet corn. *Weed Technol* **21**:206–212 (2007).

15 Mueller TC, Boswell BW, Mueller SS and Steckel LE, Dissipation of fomesafen, saflufenacil, sulfentrazone, and flumioxazin from a Tennessee Soil under field conditions. *Weed Sci* **62**:664–671 (2014).

16 Cobucci T, Prates HT, Christian L, Falcao M and Rezende MV, Effect of imazamox, fomesafen, and acifluorfen soil residue on rotational crops. *Weed Sci* **46**:258–263 (1998).

17 Weber JB, Mobility of fomesafen and atrazine in soil columns under saturated and unsaturated flow conditions. *Pestic Sci* **39**:39–46 (1993).

18 Costa AIG, Queiroz MELR, Neves AA, de Assis RC, dos Soares CES, de Oliverira AF *et al.*, Mobility and persistence of the herbicide fomesafen in soils cultivated with bean plants using SLE/LTP and HPLC/DAD. *Environ Sic Pollu Res* **22**:3457–3466 (2015).

19 USDA-NASS, *Agricultural Chemical Usage Program*. [Online]. Available: https://www.nass.usda.gov/Surveys/Guide_to_NASS_Surveys/ Chemical_Use/index.php#description [10 December 2017]

20 Culpepper AS, Moore T, Ethredge R and Briggs W, Cotton injury as influenced by herbicides, irrigation, seedling vigor, seedling depth, and environmental stresses, in *Proceedings of the Beltwide Cotton Conference*, January 3–6, National Cotton Council of America, Orlando, FL, p. 1515 (2012).

21 Everman WJ, Clewis SB, York AC and Wilcut JW, Weed control and yield with flumioxazin, fomesafen, and *S*-metolachlor systems for glufosinate-resistant cotton residual weed management. *Weed Technol* **23**:391–397 (2009).

22 Cahoon CW, York AC, Jordan DL, Everman WJ, Seagroves RW, Braswell LR *et al.*, Weed control in cotton by combinations of microencapsulated acetochlor and various residual herbicides applied preemergence. *Weed Technol* **29**:740–750 (2015).

23 Stougaard RN, Shea PJ and Martin AR, Effect of soil type and pH on adsorption, mobility and efficacy of imazaquin and imazethapyr. *Weed Sci* **38**:67–73 (1990).

24 Grey TL, Walker RH and Hancock HG, Sulfentrazone adsorption and mobility as affected by soil and pH. *Weed Sci* **45**:733–738 (1997).

25 Bowman B, Conversion of Freundlich adsorption K values to the mole fraction format and the use of SY values to express relative adsorption of pesticides. *Soil Sci Soc Am J* **46**:740–743 (1982).

26 US-EPA, *Understanding Variation in Partition Coefficient, K_d Values*. [Online]. Available: https://www.epa.gov/sites/production/files/ 2015-05/documents/402-r-99-004a.pdf [October 11 2017].

27 Kanazawa J, Relationship between the soil sorption constants for pesticides and their physicochemical properties. *Environ Toxicol Chem* **8**:477–484 (1989).

28 Savage KE and Wauchope RD, Fluometuron adsorption–desorption in soil. *Weed Sci* **22**:106–110 (1974).

29 Walker A and Jurado-Exposito M, Adsorption of isoproturon, diuron, and metsulfuron-methyl in two soils at high soil: solution ratios. *Weed Res* **38**:229–238 (1998).

30 Ferrell JA, Vencill WK, Xia K and Grey TL, Sorption and desorption of flumioxazin to soil, clay minerals and ion-exchange resin. *Pest Manag Sci* **61**:40–46 (2005).

31 Morillo E, Undabeytia T, Cabrera A, Villaverde J and Maqueda C, Effect of soil type on adsorption–desorption, mobility and activity of the herbicide norflurazon. *J Agric Food Chem* **52**:884–890 (2004).

32 Harper SS, Sorption–desorption and herbicide behavior in soil. *Rev Weed Sci* **6**:207–225 (1994).

33 Ying G and Williams B, Dissipation of herbicides in soil and grapes in a south Australian vineyard. *Agric Ecos Environ* **78**:283–289 (2000).

34 Oymada M and Kuwatsuka S, Effects of soil properties and conditions on the degradation of three diphenylether herbicides in flooded soils. *J Pestic Sci* **13**:99–105 (1988).

35 Potter TL, Bosch DD and Strickland TC, Field and laboratory dissipation of the herbicide fomesafen in the southern Atlantic Coastal Plain (USA). *J Agric Food Chem* **64**:5156–5163 (2016).

36 Schrage BW, Norsworthy JK, Smith KL, Johnson DB, Bagavathiannan MV and Riar DS, Factors contributing to cotton injury from soil-applied residual herbicides. *Summary Arkansas Cotton Res* **2012**:102–106 (2012).

37 Li X, Grey T, Vencill W, Freeman J, Price K, Cutts G *et al.*, Evaluation of cotton responses to fomesafen-based treatment applied preemergence. *Weed Technol* **32**:431–438 (2018). https://doi.org/10.1017/ wet.2018.31.

38 Kichler J and Culpepper AS, How tillage and application timing of reflex affects palmer amaranth control and cotton injury, in *Proceedings of the Beltwide Cotton Conference*, January 3–6, National Cotton Council of America, Orlando, FL, p. 1543 (2012).

39 Feng Z, Li Q, Zhang J, Zhang J, Huang X, Lu P *et al.*, Microbial degradation of fomesafen by a newly isolated strain *Pseudomonas zeshuii* BY-1 and the biochemical degradation pathway. *J Agri Food Chem* **60**:7104–7110 (2012).

40 Liang B, Lu P, LI H, Li R, LI S and Huang X, Biodegradation of fomesafen by strain *Lysinibacillus* sp. ZB-1 isolated from soil. *Chemosphere* **77**:1614–1619 (2009).

41 Grey T, Vencill W, Mantripagada N and Culpepper A, Residual herbicide dissipation from soil covered with low-density polyethylene mulch or left bare. *Weed Sci* **55**:638–643 (2007).

42 Bond W and Walker A, Aspects of herbicide activity and persistence under low level polyethylene covers. *Ann Appl Biol* **114**:133–140 (1989).