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Effect of Repeated Application of Sulfonylurea Herbicides on Sulfosulfuron Dissipation Rate in Soil

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Abstract: Accelerated microbial degradation following previous repeated applications of the same pesticide, or another pesticide of a similar chemical structure, is a known phenomenon. Currently there is limited information regarding accelerated degradation of sulfonylurea (SU) herbicides. This study is aimed to evaluate the effect of repeated SU applications on the degradation rate of the SU herbicide sulfosulfuron in soil. The effect of repeated applications of sulfosulfuron on its degradation was assessed in two soils, using a sorghum root elongation bioassay. The effect of consecutive applications of sulfonylurea herbicides over the course of three to four seasons was further examined in controlled environment and a field study. Degradation of sulfosulfuron was determined following its application to soil samples from the field or a controlled environment, by measuring sulfosulfuron residues using liquid chromatography-tandem mass spectrometry. Following the repeated application of sulfosulfuron in the bioassay, the time to reduce sorghum root growth by 50% was shortened by up to 31.6%. However, consecutive application of SUs in the controlled environment had no effect on sulfosulfuron degradation rate constant. Yet, sulfosulfuron degradation rate was enhanced by a factor of 1.35 following consecutive application of SUs in the field, compared to untreated control soil. The data confirm that sulfosulfuron degradation could be enhanced due to repeated sulfosulfuron applications, thus potentially reducing its herbicidal efficacy.

Keywords: accelerated degradation; enhanced degradation; residual herbicides; cross enhancement

1. Introduction

Sulfonylurea (SU) is a group of herbicides which inhibit the biosynthesis of branched-chain amino acids in plants, through inhibition of the enzyme acetolactate synthase (ALS) [1]. These herbicides are widely used worldwide for selective weed control in various field-crops (e.g., wheat, cotton, oil seed rape, alfalfa and corn), orchards (such olive groves) and vegetables (including tomato and potato) in pre-planting and post-planting applications [2–6]. Some of these herbicides are known to be highly persistent in the soil, with a long-term residual activity that results in damage to sensitive plants for up to several years after application to the soil [7–9]. Sulfosulfuron, a SU herbicide, is a residual herbicide used primarily for selective weed control in wheat [10] but also for selective control of *Phelipanche* spp. in tomato [11,12].

Degradation of SUs in soil is known to be pH dependent. Their persistence in acidic soils is relatively low due to rapid chemical hydrolysis, while in neutral- to low-alkaline soils chemical hydrolysis is slow, hence persistence is higher, and microbial breakdown is considered to be the

main mechanism of degradation [1,13]. Multiple microorganisms, including fungi, bacteria and actinomycetes, isolated from SU-contaminated soils, are able to degrade SUs and use them as a sole carbon or nitrogen source [14–22]; specifically, Yadav and Choudhury [14] and Arya et al. [15] isolated strains of *Trichoderma* sp. and *Brevibacillus borstelensis*, respectively, that are able to degrade sulfosulfuron. In some reports on isolation of microorganisms from SU-contaminated soils, inoculation of fresh or sterilized (autoclaved) non-contaminated soil with SU-degrading microbial strains reduced the persistence of SU herbicide in the soil [17–19,22], illustrating a potential enhancement of degradation rates due to changes in soil microbial community.

Increased degradation rates of biodegradable pesticides due to changes in the soil microbial community, has been shown to occur in response to repeated application of a specific pesticide, or applications of other pesticides from the same chemical group—referred to in the scientific literature as "accelerated degradation" or "enhanced degradation" [23]. Arbelli and Fuentes [23] have summarized numerous cases of enhanced pesticide degradation, including fungicides, nematicides, soil fumigants and herbicides; in many of these cases the outcome is loss or reduced efficacy of the soil-applied pesticide. Enhanced degradation of herbicides has been previously reported for several herbicides from different chemical groups, including multiple cases of triazines (e.g., atrazine and simazine) [24–27], thiocarbamates (e.g., EPTC, vernolate and butylate) [28–32] diphenyl heterocycles (i.e., fluridone) [33] and phenylureas (e.g., diuron, isoproturon and linuron) [34–37]. Data regarding the possible enhanced degradation of SUs, on the other hand, is limited and includes, to the best of our knowledge, only three individual cases of enhanced degradation rates due to repeated application: degradation of chlorsulfuron in Brazilian Oxisols [38], degradation of bensulfuron-methyl in soil sampled from paddy-rice fields in China [39] and degradation of triasulfuron in an Inceptisol in Spain [40]. In these studies, degradation rates were enhanced by a factor ranging between 1.3 and 3.0.

The current reduction of SU herbicides that are available for use by farmers, due to evolution of ALS-resistant weeds and the ban of many herbicides due to stricter regulation [41–44], emphasizes the concern associated with enhanced herbicide degradation that results in reduced weed control efficacy. Thus, the aim of the present study is to estimate the effect of SU application history on the degradation rate of sulfosulfuron in soil. In Israel, sulfosulfuron is used primarily for control of the root parasitic weed Egyptian broomrape (*Phelipanche aegyptiaca* (Pers.) Pomel) in open field tomato, which, according to local crop rotation, is cultivated every 3 to 5 years. Between applications of sulfosulfuron, other SUs may be used for weed control. Hence, the objectives of the current study were to (a) estimate the effect of repeated sulfosulfuron application on its residual activity in soil and (b) to estimate the effect of consecutive applications of other SUs, commonly used in Israeli crop rotation, on sulfosulfuron degradation rates in soil.

2. Materials and Methods

2.1. Types of Soils

Four soils from different sites were collected for the current study. Soil was sampled from the top 0–10 cm of two field plots, Havat (H.) Eden and Kalanit, at Beit She'an valley and Hula Valley (northern Israel), respectively, as described in a previous paper [9], to evaluate the effect of repeated sulfosulfuron application on its residual activity in soil. To study the effect of repeated SU application in a controlled environment, soil was sampled from a field plot in Newe Ya'ar Research Center (Jezre'el valley, northern Israel) in which no herbicides had been applied in the last 15 years. A batch of 200 kg soil was sampled from the top 0–30 cm and subsequently air dried, passed through a 10 mm sieve and thoroughly mixed. Finally, to study the effect of repeated SU applications under field conditions, a field study was conducted at Newe Ya'ar Research Center. The above four soils were characterized as clayey soils, with low-alkaline pH, low organic matter content and varied $CaCO_3$ content (Table 1).

Table 1. Selected properties of the soils used in this study.

Soil Source	GPS Coordinates	pH	Organic Matter (%)	Sand (%)	Silt (%)	Clay (%)	CaCO$_3$ (%)
H. Eden	32°28′01.2″ N 35°29′27.6″ E	7.8	1.9	18.8	31.8	49.5	41.3
Kalanit	33°10′48.0″ N 35°36′21.6″ E	7.6	1.7	16.6	34.6	48.9	23.4
Newe Ya'ar (Controlled environment)	32°42′13.6″ N 35°11′05.7″ E	7.5	2.0	15.2	26.3	58.6	12.5
Newe Ya'ar (Field)	32°42′30.4″ N 35°10′40.1″ E	7.9	2.7	20.6	24.7	54.7	22.9

2.2. Sulfosulfuron Residual Activity in Soil

The residual activity of sulfosulfuron in soil samples from Kalanit and H. Eden (Table 1) was quantified using a root-elongation bioassay commonly used to determine the effect of soil-applied herbicides on plants [45]. In the current study sorghum (*Sorghum bicolor* (L.) Moench.) hybrid STT12 (Sorghum Partners, Lubbock, TX, USA) was used as the test plant, to monitor the decline in residual activity with incubation time, as described in a previous paper [9]. In that study the residual activity of sulfosulfuron was monitored in soil samples collected from the clayey soils of Kalanit and H. Eden, after application of sulfosulfuron (80 ng·g^{-1}) and up to the point where no residual activity was detected (i.e., non-significant inhibition of sorghum root elongation). The current study examined the effect of a second application of sulfosulfuron (Monitor WG, 75% ai, Monsanto, St. Louis, Mo, USA) to the same soil samples. For that, following the full disappearance of residual phytotoxicity, the samples were air dried, passed through a 4 mm sieve and treated again with an aqueous solution of sulfosulfuron to achieve the same initial conditions as in the first application: a concentration of 80 ng·g^{-1} and soil moisture of 70% of field capacity [9]. The same procedure was applied to the untreated control samples, except that only deionized water was used instead of the herbicide solution. After herbicide application, the soil was thoroughly mixed and repacked into ten replicate 10 × 10 cm square petri-dishes (Sterilin, Thermo Scientific, Waltham, MA, USA), to monitor the residual activity during incubation at 25 °C by using the sorghum bioassay as previously described [9]. Briefly, sorghum was sown in the petri dishes following different incubation periods, and the root length was measured four days after sowing. Considering an earlier observation that maximal inhibition of root elongation in this bioassay was 85%, the root elongation data were normalized to percentage phytotoxicity, using the following equation:

$$Y = 100 \times \frac{I}{85} \tag{1}$$

where *Y* is the normalized phytotoxicity (%) and *I* is the measured inhibition of sorghum root elongation following sulfosulfuron application (%) relative to the untreated control.

2.3. Multi-Year Sulfonylurea Application Experiments

Field and controlled environment experiments included six treatments, each of them was based on a specific combination of three-year applications (controlled environment) or four-year applications (field) of assorted SU herbicides. Combinations were designed to represent common SU herbicides used by Israeli farmers and different rates of applications. Additionally, a control treatment was included, in which no SU herbicide was applied throughout the experiment. Detailed SU application rates and timings are given in Table 2. In both experiments (controlled environment and field), herbicides were applied with a motorized sprayer, delivering 200 L·ha^{-1} at 300 kPa, equipped with a Tee Jet 8001E nozzle (Spraying Systems Co., Glendale Heights, IL, USA). In all these treatments, commercial

formulations of the herbicides were used; details of each formulation are presented in the Supplemental Data (Table S1).

Table 2. Multi-year schemes of sulfonylurea treatments in a controlled environment and in the field.

Date	Herbicide	T0	T1	T2	T3	T4	T5	T6
		Application Rate (g ha^{-1})						
5 July 2015	Foramsulfuron	0	45	45	45	45	45	45
7 July 2015	Rimsulfuron	0	0	0	0	12.5	12.5	12.5
22 May 2016	Trifloxysulfuron	0	12.2	12.2	12.2	22.5	22.5	22.5
13 December 2016	**Sulfosulfuron**	0	22.5	22.5	0	37.5	37.5	0
13 December 2016	Chlorsulfuron	0	0	0	12.5	0	0	15
22 March 2018	**Sulfosulfuron**	0	56.2	0	0	56.2	37.5	0
29 April 2018	**Sulfosulfuron**	0	37.5	0	0	37.5	0	0
29 April 2018	Rimsulfuron	0	0	12.5	12.5	0	25	25
20 May 2019	**Sulfosulfuron**	0	0	0	0	37.5	0	0
20 May 2019	Rimsulfuron	0	0	0	0	0	25	25

2.3.1. Sulfonylurea Treatments in Controlled Environment

Herbicides were applied to 5 kg soil, packed in 10 L buckets, with five replicate buckets per treatment (Table 2). After application, the soil was watered with deionized water, to reach 70% of field capacity, before being transferred for incubation in a ventilated dark room. The hourly temperature was recorded in the incubation room throughout the experiment using a data logger (HOBO Pendant temperature/light data logger, Onset Computer, Bourne, MA, USA) and the mean recorded daily temperature was 22 °C (±1.5 °C) (Figure S2). Soil moisture was corrected monthly (by weight) to compensate for water loss by evaporation. Initial measurements showed that between rewetting intervals the soil water content reached a minimum of 50% of field capacity (data not shown).

2.3.2. Sulfonylurea Treatments in the Field

The experimental field was divided into 35 plots of 4.6 m^2 size (2.3 × 2 m). Seven treatments of annual SU applications were examined in five replicate plots, distributed in a complete random design. Within the four years of the experiment, crops were rotated according to the common practices used in irrigated farms in this region. Corn was cultivated in the first year, followed by cotton, wheat and tomatoes (Table 3). In each growing season, herbicides were applied according to the specific program of each treatment (Table 2). To minimize weed interference, the herbicides glyphosate and glufosinate were uniformly applied to the whole plot between growing seasons. Both herbicides are considered non-residual, belong to chemical groups different than SU, and are thus unlikely to affect sulfosulfuron degradation in soil. Plots were rototilled and leveled before maize was sown and before tomato was transplanted; otherwise, the plots were managed with no-tillage throughout the experiment, to minimize soil transfer between sub-plots.

Table 3. Crop rotation in the experimental field.

Crop	Planting Date	Harvest Date
Corn	21 June 2015	1 September 2015
Cotton	12 April 2016	2 November 2016
Wheat	30 November 2016	1 June 2017
Tomato	9 April 2018	18 July 2018

2.4. Determination of Sulfosulfuron Degradation Rates

Soil (approximately 200 g) was sampled on 31 March 2019 (257 days after the last herbicide application) from the top 0–10 cm layer of each bucket (controlled environment study) and plot (field study). In the field, the soil was sampled from the middle of each plot. Each soil sample was thoroughly mixed, air dried in a ventilated room for 72 h and immediately used for the determination of sulfosulfuron degradation rate as follows: Sulfosulfuron—(MON35700, 99.9% sulfosulfuron, Monsanto Ltd., Creve Coeur, MO, USA) stock solution (375 ng mL^{-1}) was prepared by dissolving the herbicide in deionized water. Then, 50 subsamples, of 5 g air-dried soil each, were weighed out of each of the soil treatments, transferred into 20 mL vials and fortified with 1.2 mL aliquots of the herbicide stock solution. After herbicide application, the vials were capped and incubated in the dark at 25 °C for a period of 42 days, ventilating it twice a week by removing the cap for 20 min. Preliminary soil respiration tests showed that such ventilation intervals are sufficient to maintain aerobic conditions (data not shown). After incubation of 0, 14, 28 or 42 days, five replicates from each soil sample were taken for extraction and determination of sulfosulfuron concentrations as described in a previous publication [9]. Briefly, sulfosulfuron was extracted in 8 mL of 4:1 methanol:water solution, by shaking for 16 h in a horizontal shaker. The herbicide concentration in the soil extract was quantified using liquid chromatography–tandem mass spectrometry (LCMS-MS), with a 99% recovery rate and a limit of detection of 2.7 ng sulfosulfuron g^{-1} dry soil.

2.5. Statistical Analysis

A non-linear regression was facilitated by SigmaPlot 14.0 (Systat Software Inc., San Jose, CA, USA) to fit a curve describing sulfosulfuron residual activity with time in the soil bioassay, using a three-parameter log-logistic sigmoidal equation:

$$Y = \frac{a}{1 + \left(\frac{X}{X_0}\right)^{-B}} \tag{2}$$

where Y represents the phytotoxicity to sorghum (%) at time X (day); a is the upper asymptote representing the normalized (Equation (1)) maximum phytotoxicity in the soil at time 0 (%); X_0 is the inflection point, representing the time (day) to reach 50% reduction of maximum phytotoxicity; and B represents the slope at the inflection point. To determine whether the dynamics of the decline in phytotoxicity with time following the second sulfosulfuron application differs from the dynamics following the first application, an F-test was performed [46]. The null-hypothesis was that an individual non-linear regression for each treatment does not differ from the regression obtained for the combined data set (second and first herbicide application cycles) (p-value < 0.05). Hence, the residual sum of squares of the combined data set regression ($S1$) and the residual sum of squares of each individual data set regression ($S2$ and $S3$) were obtained. Subsequently, F value was calculated using the following equation:

$$F(p, n1 + n2 - 2p) = \frac{S5/p}{S4(n1 + n2 - 2p)} \tag{3}$$

where $S5 = S1 - S4$; p is the number of regression parameters; $S4 = S2 + S3$; $n1$ is the number of data points in the first individual regression model and $n2$ is the number of data points in the second individual regression model. The output F value was computed using the F.DIST function in Microsoft Excel, which returns the F probability distribution.

Sulfosulfuron degradation in soil, following annual SU application, was also analyzed using a non-linear regression facilitated by SigmaPlot 14.0. Based on previous reports on sulfosulfuron degradation in soil [9,47,48], first-order kinetics was assumed. Hence, to quantify the first-order

degradation rate constant, in soils from the field or controlled environment study, data of sulfosulfuron concentration in soil were regressed using a two-parameter exponential decay equation:

$$Y = C_0 \times e^{-KX} \tag{4}$$

where Y is sulfosulfuron relative concentration, C/C_0 (%) at time X (day); C_0 is the initial concentration (%); and K is the first-order degradation rate constant (day^{-1}). In each experiment, the regression model was fitted to the whole data set and to each individual data set. Additionally, the regression model was fitted to the whole data set, excluding the data of each treatment one at a time. To determine whether the regression model of each of the seven SU application configurations, in the controlled environment or field study, should be analyzed separately from the regression model of the whole data set, an F-test was performed, as mentioned above, with the null-hypothesis that the regression of each individual data set does not differ from the regression of the whole data set.

In 2015, SU treatments were applied only in the field. Additionally, all treatments (T0–T6) in the field, included the application of either glyphosate or glufosinate, in the time between growing seasons, to reduce weed interference.

3. Results

3.1. Sulfosulfuron Residual Activity Following Repeated Application to Soil

The residual activity of sulfosulfuron was monitored following a second application of the herbicide in two soils. Results of the residual activity following the first application in these soils were presented and discussed in a previous publication [9]. Briefly, the data revealed that phytotoxicity to sorghum, following sulfosulfuron application (80 ng·g^{-1} soil), declined more rapidly in the soil from H. Eden compared to the soil from Kalanit. Based on a non-linear three-parameter log-logistic sigmoidal regression (Equation (2)), the time required after treatment to reach 50% reduction of maximum phytotoxicity (X_0) was estimated as 54.2 and 105.0 days, in the soil from H. Eden and Kalanit, respectively (discussed previously; [9]). In the current study, a similar trend was observed following a second sulfosulfuron application to the same soil samples (Figure 1; Table 3). In this case, the results of an F-test indicate that regression analysis of the first and second application cycles differ significantly from regression analysis of the combined data set, in soil from H. Eden ($p(F) = 0.0457$) and from Kalanit ($p(F) < 0.0005$) (Table S2). As for the second application, the estimated X_0 (±SE) in H. Eden soil—a measure of sulfosulfuron residual activity period—was 41.7 days (±4.7), a 23.2% reduction from the estimation in the first application cycle (Figure 1a). In the soil from Kalanit, the decline in estimated X_0 was more prominent, with an estimated X_0 of 71.8 days (±4.7) (Table 3 and Figure 1b), a 31.6% decline in the period of sulfosulfuron residual activity due to repeated application of the herbicide.
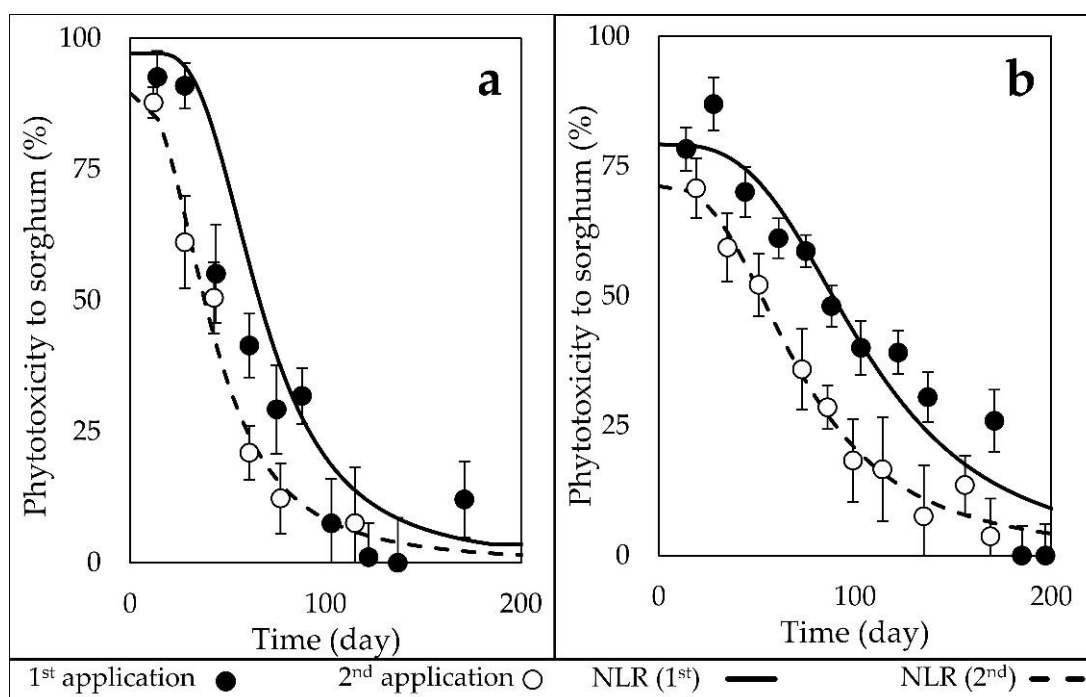
Figure 1. The effect of repeated sulfosulfuron application on the dynamics of its residual activity in soil from H. Eden (**a**) and Kalanit (**b**), as measured by sorghum root elongation. Sorghum root length was measured four days after sowing, and phytotoxicity was calculated using Equation (1). Results of the first sulfosulfuron application were presented in a previous publication [9]. A second sulfosulfuron application was performed immediately after termination of the first application experiment, and a non-linear regression was fitted to the data (Table S2). Error bars represent the standard error (n = 10). NLR = Non-linear regression.

3.2. Sulfosulfuron Degradation in Soil Following Multi-Year Sulfonylureas Application

The effect of consecutive applications of SU herbicides on the rate of sulfosulfuron degradation was evaluated in soil samples that were treated over 3–4 years with SU herbicides, to create different herbicide application history (Table 2). Sulfosulfuron concentration was monitored for a period of 42 days following its application to soil samples from a controlled environment study (Figure 2a) and a field study (Figure 2b). In samples from the controlled environment study, sulfosulfuron degradation rate was similar in all treatments, including non-SU-treated control, and at 42 days after treatment the minimum measured concentration (±SE) was 40.3% (±3.6) of the initial concentration (Figure 2a). In the samples from the experimental field, sulfosulfuron degradation was faster, compared to the degradation in samples from the controlled environment, reaching a minimum measured concentration (±SE) of 15.9% (±5.9) of the initial concentration (Figure 2b). Moreover, in this experiment the degradation was faster in the SU-treated samples (T1–T6) compared to the non-SU-treated control (T0).
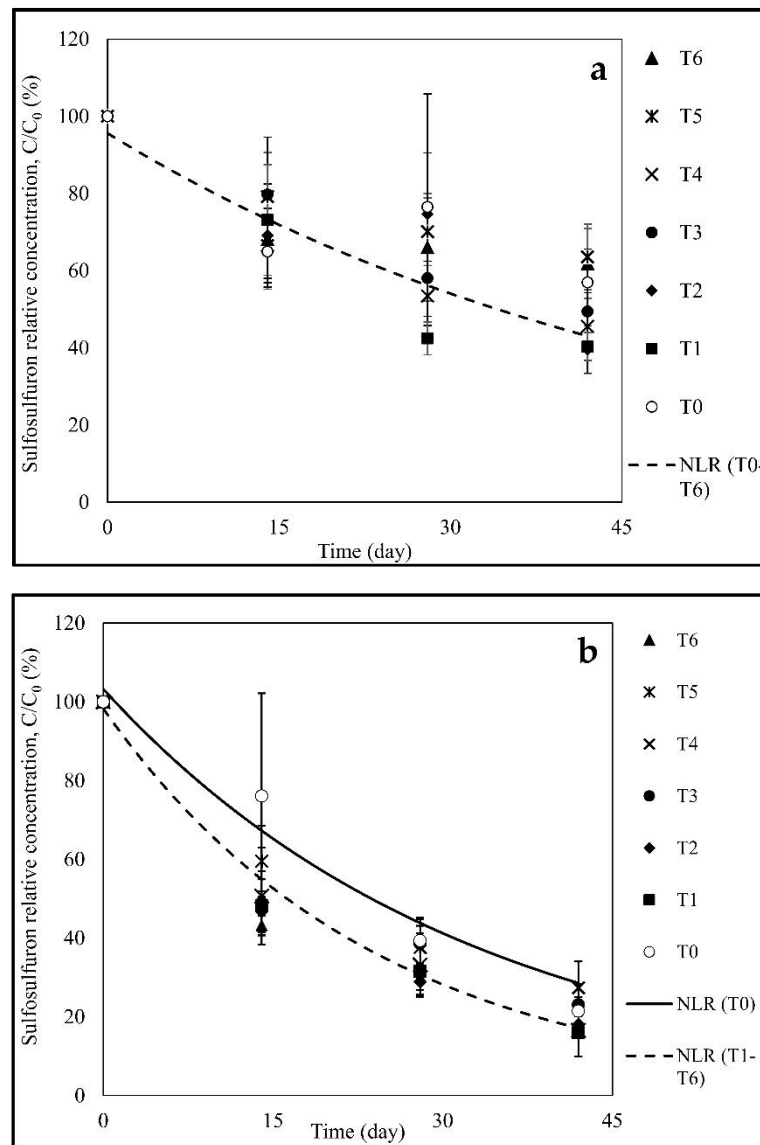
Figure 2. Degradation of sulfosulfuron in soil samples with different history of sulfonylurea application in a controlled environment (**a**) and in the field (**b**). Sulfosulfuron concentration (*C*) was quantified in soil extract using liquid chromatography–tandem mass spectrometry (LCMS-MS) and presented as a percentage of the initial measured concentration (C_0). Details of SU application rate and timings are given in Table 2. An exponential decay non-linear regression (NLR) was fitted to the data of relative sulfosulfuron concentration, C/C_0 (Table S3 and Table S4 for controlled environment and field, respectively); treatment data are grouped in one regression analysis based on the F-test applied to each treatment versus the grouped data (Equation (3)). Error bars represent the standard error (*n* = 5). NLR = Non-linear regression.

An exponential decay equation (Equation (4))—representing a first-order kinetics—was fitted to degradation of sulfosulfuron in soil samples with a different SU application history (Figure 2a,b). Regression analysis (Equation (3)) of sulfosulfuron degradation, in soil with different SU application history in a controlled environment, showed that regression of each individual data set did not differ significantly from the regression of the whole data set (Table S3), indicating that the SU treatments did not have a significant effect on the degradation rate of sulfosulfuron; hence, only the regression of the whole data set is presented (Figure 2a). Regression analysis of degradation in samples with different application history in the field, however, revealed that the non-SU-treated control (T0) was

significantly different from the regression of the whole data set (p(F) = 0.012), demonstrating a difference in degradation kinetics (Table S4). The estimated degradation rate constant, K, (±SE) in the SU-treated samples was 0.042 day^{-1} (±0.002), a 1.35-fold increase from the estimated 0.031 day^{-1} (±0.007) in the T0 samples, indicating a potential for enhanced degradation of sulfosulfuron due to the repeated application of SU herbicides.

4. Discussion

The acceleration of herbicide degradation rates in soil following repeated applications (i.e., enhanced degradation rate) is well documented [22–37]. Results from the current study reveal a potential for enhanced sulfosulfuron degradation rates in soil, most likely due to accelerated biodegradation by soil microorganisms. This potential is demonstrated by up to a 31.6% decrease in the time to reach a 50% reduction of maximum sulfosulfuron phytotoxicity (X_0), following repeated sulfosulfuron application (Figure 1b), and a 1.35 enhancement factor (i.e., factor by which degradation rate constant increased) following annual SU application over a four-year period (Figure 2b). These results are in the low range of the previously reported effect of repeated SU applications: Xie et al. found a 1.8 enhancement factor of bensulfuron-methyl degradation, following a second application, and a substantial reduction in its residual activity period [39]; García-Delgado et al. reported an increased degradation rate of another SU herbicide (triasulfuron) following its repeated application, with the enhancement factor ranging between 1.34 and 3.00, depending on irrigation and compost treatments [40]; finally, Ravelli et al., who studied chlorsulfuron degradation in soil, found a 1.3 enhancement factor following its repeated application [38]. Reports on enhanced degradation of other herbicides also show a more notable effect of repeated application. Lee et al. revealed that EPTC half-life was reduced by an estimated factor of 1.63 to 3.19 following its repeated application [29] and Walker and Welch reported a factor of 3.38, 4.74 and 5.71 increase in the first-order degradation rate constant, following repeated applications of the herbicides alachlor, propyzamide and linuron, respectively [34]. Moreover, in a study on the spread of enhanced atrazine degradation in the US, Mueller et al. reported an enhanced degradation rate of atrazine, in soil with a history of atrazine application, by a factor of 43.4 [25]; however it is worth noting that a wide range of enhancement factors were measured in the 60 history soils surveyed in that study, including cases in which atrazine degradation rate was not enhanced.

In the current study, consecutive annual SU application in the field enhanced sulfosulfuron first-order degradation rate constant, but no clear trend was found regarding the effect of specific SU treatments and rates (Figure 2b). The herbicide doses were selected to represent the possible low-end (T1–T3) and high-end (T4–T6) doses used by Israeli farmers, according to common practices and the recommended dose in local herbicide labels; given the relatively small effect that SU treatments had on the enhancement of sulfosulfuron degradation rate, it is likely that the differences between doses would be too low to induce significant variation between treatments. Consecutive annual SU application also resulted in enhanced sulfosulfuron degradation rate in soil samples which were not exposed to sulfosulfuron throughout the study, indicating a potential for cross enhancement. Cross enhancement, which involves an enhanced degradation of a pesticide in soil that was induced by previous applications of other pesticides of the same chemical family [24], has been reported in different herbicide groups, including thiocarbamates [29,31] and triazines [24]. Our results show an enhanced sulfosulfuron degradation rate in SU treatments T3 and T6, which did not include sulfosulfuron (Figure 2b), possibly indicating a broad specificity of the degrading microorganisms [23].

An interesting observation, not related to repeated application of SU herbicides, was the significantly and substantially higher sulfosulfuron degradation rate constants in soil sampled from the field (Figure 2b) compared to the controlled environment (Figure 2a). In a 3–4 years experiment, it is unlikely that the application of SU on year 2015, that was not included in the controlled environment setup, is the source for the higher degradation rate in the SU history soils from the field. It is more likely that these differences reflect the intrinsic variation of sulfosulfuron degradation rates in the soils,

derived from soil properties such as pH, $CaCO_3$ or organic matter content (Table 1), all previously linked to varied degradation rates of pesticides in soil [1,49–51]. In addition to the effect of soil properties, it is very likely that the long-term effect of the different incubation conditions—i.e., incubation under controlled and relatively constant conditions (Figure S1) with no vegetation, versus field conditions (Figure S2) under crop rotation—had a substantial effect on soil microbiome and consequently on the biodegradation of sulfosulfuron [52]. Specifically, the effect of vegetation on soil microbiome may have contributed to the faster sulfosulfuron degradation rate in soil from the field, as several studies showed higher degradation rates of pesticides in soil sampled from a planted site compared to degradation rates in bare soil [28,53–55].

Enhanced degradation rate of sulfosulfuron may have a meaningful agronomical and environmental impact. Arbelli and Fuentes [23] listed at least nine herbicides for which loss of herbicidal efficacy due to enhanced degradation was reported. Moreover, Mueller et al., who surveyed the spread of enhanced atrazine degradation in the US, concluded that the widely used herbicide might no longer be effective for long-term weed control in the majority of 60 sampled history soils [25]. Figure 3 illustrates the effect of enhanced sulfosulfuron degradation rates and the predicted concentration of sulfosulfuron in soil, considering three scenarios based on the results of the current study: Scenario 1 considers the possibility that degradation rate constant K is equal in soil with no SU application history (K_{NH}) and in soil with a history (K_H), as data show that K_{NH} upper 95% confidence interval (CI) overlaps the K_H lower 95% CI. Hence, in this scenario sulfosulfuron degradation rate is not enhanced and naturally weed control efficacy will not be affected. Scenario 2 considers a 1.35-fold increase in degradation rate constant in history soils, as estimated by the mean K value in the field study (Figure 2a; $K_{NH} = 0.032$ day^{-1}, $K_H = 0.042$ day^{-1}), which would potentially reduce concentrations of sulfosulfuron at 50, 100, 200 and 300 days after application by a factor of 1.7, 3.0, 9.0 and 27.1, respectively (Figure 3b). These differences could affect weed control efficacy throughout the season in specific cases, such as sulfosulfuron pre-planting incorporation for control of Egyptian broomrape in tomato [9], but more prominently could reduce the potential injury to rotational crops [4,8] and the risk for pollution of below and above ground water reservoirs due to herbicide leaching, considering the lower herbicide persistence [24]. Finally, scenario 3 considers the possibility that K_{NH} is equal to the lower 95% CI (0.016 day^{-1}) and K_H equals to the upper 95% CI (0.045 day^{-1}), in which case sulfosulfuron degradation rate constant enhances by a factor of 2.81-fold, which could reduce sulfosulfuron concentrations at 50, 100, 200 and 300 days after application by a factor of 4.3, 18.2, 330 and 6000, respectively. Such a reduction in concentration is expected to decrease the overall residual weed control efficacy [3,5] but also reduce the negative long-term effects of the herbicide persistence (i.e., reduce potential injury to rotational crops). This scenario analysis is a rough estimation of the enhanced degradation rate effect, since it does not account for possible variation in temperature and moisture dependencies of sulfosulfuron degradation rates in the different soils [9,56], nor does it account for the effect of precipitation on transport of the herbicide in the soil profile [57], all of which could further affect herbicide persistence and residual activity.
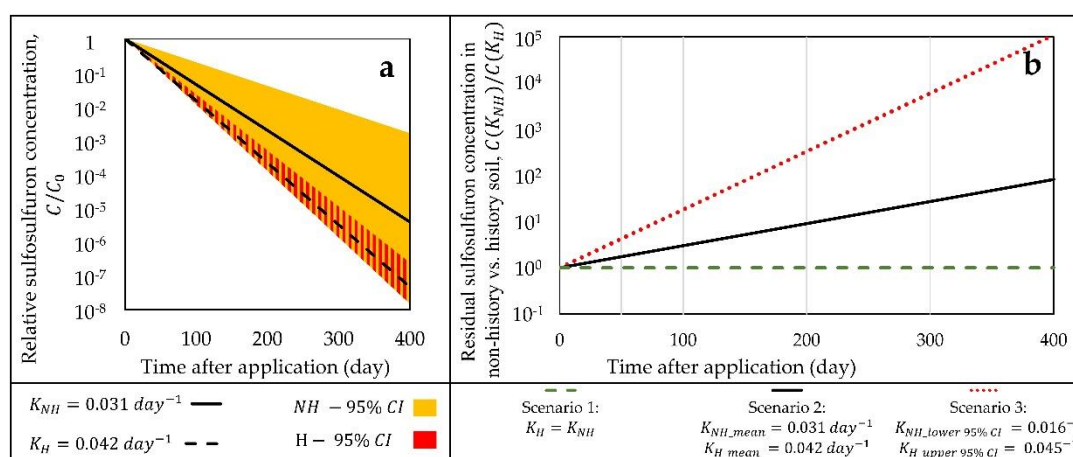
Figure 3. Dissipation of sulfosulfuron in soils considering different first-order degradation rate constant (*K*) (**a**) and the resultant variation in residual sulfosulfuron concentrations in soil (**b**). Concentration after application was calculated using Equation (4) substituting *K* with estimated values in the field experiment, ±95% confidence interval (CI) (Table S4).

5. Conclusions

Sulfosulfuron degradation rate is potentially enhanced in soil with a history of SU use in the field, most likely due to acceleration of its biodegradation by soil microorganisms. These findings support the currently limited information available on this phenomenon in SU herbicides. Though the estimated enhancement factor is relatively low based on this study, the results of such an enhancement may still lead to substantial variation in sulfosulfuron persistence in soil, which in turn could affect its residual activity in weed control. The widespread use of SU herbicides in different crops makes this group vulnerable to enhanced degradation rates due to adaptation of soil microorganisms. Thus, further work is needed to determine the extent of SUs enhanced degradation, including surveys in a wide range of soil types and environmental conditions, testing of different configurations of SU applications history and examination of possible enhancement of degradation rate of other SUs.

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