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Soil residues of sulfosulfuron herbicide in wheat field determined by bioassay and laboratory methods

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Abstract: Although herbicides are used for weed control in the field, their residues can have unfavourable environmental impacts. The objective was to determine the sulfosulfuron herbicide residues in wheat field soil using bioassay and laboratory (HPLC) methods. The two-year experiment was a randomised complete-block design (RCBD) with three replicates using herbicide at control, recommended (26.6 g/ha, D1) and doubled (53.2 g/ha, D2) rates. Soil samples (0–10 cm) were collected randomly at intervals ranging from 0 to 125 days after spraying. Greenhouse experiments (bioassay method) with eight plant species indicated garden cress (*Lepidium sativum* L.) and corn (*Zea mays* L.) as the most and the least sensitive ones, respectively. The herbicide residues were stable at D1 up to 90 days after herbicide use, at 1.41 and 0.52 µg/kg in 2019 and 2020, respectively. However, 125 days after herbicide use no residues were observed. With time and for both treatments, soil herbicide residues decreased or the percentage of herbicide loss increased. The sensitivity of HPLC method to detect the herbicide residues was less than the bioassay method. The three-parameter sigmoid equation indicated the mean of DT_{50} for D1, averaged for the two years it was 19 days.

Keywords: herbicide persistence; model fitting; plant sensitivity

Although wheat is one of the most important sources of food and nutrients in the world, its growth and yield is reduced by weeds (Saeedipour and Saeedi 2020). In the last three decades, the weeds of wheat fields have been mainly controlled by herbicides such as sulfosulfuron (brand name: Apirus, WG 75%), which is a selective herbicide of the sulfonylurea group used for controlling broad and narrow-leaved weeds (Ghafarpour et al. 2018).

Sulfosulfuron is absorbed through leaves and roots and can be transmitted through apoplasts and symplasts, and eventually stops plant growth. It has a water-soluble granule formulation with the solubility of 26.6 g/ha (with a non-ionic surfactant such as sitogit) (Paporisch et al. 2020). Sulfosulfuron must be used in combination with a non-ionic surfactant such as sitogit from the beginning to the end of wheat tillering (Joshi et al. 2019).

However, the sulfonylurea herbicides remain active after being applied to the soil (Paul and George 2021) extending their weed control potential (Pannell et al. 2016). Accordingly, increasing herbicide stability in the soil may damage crops over the next years (Sheikhhasan et al. 2012, Davis and Frisvold 2017, Mohapatra et al. 2021), which is also of environmental concern. Therefore, the use of environmentally friendly methods for weed control has been extensively researched (Brar and Gill 2021, Martins-Gomes et al. 2022).

Accordingly, knowing the herbicides stability in the soil seems so necessary to determine herbicides potential in polluting the environment and damaging crops (Zobir et al. 2021). Robinson and McNaughton (2012) investigated the damage caused by the residues of saflufenacil herbicide (100 and 200 g/ha) on different crops (cabbage, carrots, cucumbers, onions, peas, peppers, potatoes, and sugar beets). Plants had different sensitivity as potatoes and chickpeas grew in the year after herbicide application, but cabbage, carrots, cucumbers, onions, peppers and sugar beets did not. Yousefi et al. (2016) examined the half-life of sulfosulfuron herbicide in conventional tillage (reversible plough and two-time disc) and no-till systems using high-performance liquid chromatography, and found that the decreasing trend of sulfosulfuron

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herbicide followed a first-order kinetic equation over time. Sulfosulfuron herbicide was significantly reduced under the two tillage methods, with a higher reduction in the no-till treatment. The shelf life of sulfosulfuron in the no-till treatment with half-life of 4.62 days was less than the conventional tillage treatment (6.3 days).

With respect to the above-mentioned details, and the significance of investigating the persistence of sulfosulfuron herbicide in the soil of wheat fields, the present research was conducted. The objective was to determine the sulfosulfuron herbicide residues in wheat field soil using bioassay and laboratory methods.

MATERIAL AND METHODS

The wheat research field is located in the Varamin city (2 431 km^2, 35°30'N and 51°30'E), Iran, with the altitude of 750 to 900 m a.s.l. Based on the soil taxonomy method, soil type of this region is Aridisol. Soil physicochemical properties including texture, salinity, pH, organic carbon, calcium carbonate, N, P and K were determined using the standard methods (Miransari et al. 2008, Table 1).

Experimental design. The two-year (2019 (Y1) and 2020 (Y2) experiment, conducted in a 1 500-m^2 wheat field, was a randomised complete block design with three replicates (5 m apart). The plots (0.5 m apart) measuring 30 m^2 (10 × 3 m) consisted of ten 6-m rows with a 20-cm distance (planted at 72 000 plants per hectare). The sulfosulfuron herbicide (75% DF prepared by the Bazargan Kala Company) was applied at control, recommended (D1) and doubled amounts (D2) using 26.6 and 53.2 g/ha of active ingredient per litre per hectare, respectively by the Matabi knapsack sprayer (model: Elegance, Taizhou, China) with uniform blowing nozzle at 2.8 bar pressure. The wheat plants were treated with the herbicide in the tillering stage (stage 22 according to the BBCH scale). The field was fertilised with urea (150 kg/ha) at planting, tillering, and plant stemming stage and with ammonium phosphate (250 kg/ha) during planting. There were no specific pests and diseases during the experiment, and so no pesticides were used.

Herbicide measurement. Soil samples were collected randomly from a depth of 0–10 cm (soil surface) using auger at intervals of 0 (S1), 3 (S2), 10 (S3), 20 (S4), 30 (S5), 60 (S6), 90 (S7) and 125 (S8) days after spraying. The samples were mixed and dried after transferring to the laboratory, passed through a 2-mm sieve and kept at –20 °C for further analyses. The amount of soil herbicide was determined according to Srivastava et al. (2006).

The soil sample (50 g) was treated with acetonitrile and ammonium carbonate 1 mol/L (1:9 *v*/*v*) and was shaken (30 min). The supernatant was collected, and the solution was re-shaken and the volume of the new supernatant with the previously collected supernatant was reduced to 20 mL by rotary evaporator. The solution was treated with 50 mL NaOH (1 mol/L) and the supernatant was collected using a funnel and 50 mL methylene chloride, and was demoisturised with Na_2SO_4 to reduce its volume to almost nil. The collected powder was treated with 2 mL acetonitrile, filtered (0.45 μm), and was then injected to the column of HPLC (Model Platin Blue, equipped with photodiode detector).

Bioassay method. Greenhouse experiments tested the sensitivity (root and shoot growth) of plant species including lentil (*Lens culinaris* Medik.), sugar beet (*Beta vulgaris* L.), mung bean (*Vigna radiata* L.), garden cress (*Lepidium sativum* L.), cucumber (*Cucumis sativus* L.), corn (*Zea mays* L.), canola (*Brassica rapa* L.) as well as chickpea (*Cicer arietinum* L.) to soil sulfosulfuron residues (Paul et al. 2009) (Figures 1 and 2). Accordingly, pots measuring 10 × 10 cm, were filled with the treated soil (500 g) (contaminated with the herbicide).

Statistical analyses. The three-parameter sigmoid equation in SigmaPlot 12 (Systat Software, Inc., San Jose, USA) was used to determine DT_{50} (time required to decompose 50% of herbicide = herbicide half-life).

$$f = a/(1 + \exp(-(X - X_0)/b) \quad (1)$$

Where: a – maximum herbicide loss; X_0 – time required to lose 50% of the herbicide; b – slope of increasing or decreasing the herbicide loss per one day.

Table 1. Soil physicochemical properties

Texture	Sand	Silt	Clay	EC	pH	OC	$CaCO_3$	N	P	K
	(%)			(dS/m)		(%)		(mg/kg)		
Loam	32.0	45.3	22.7	1.60	8.3	0.46	30.0	0.079	20.2	280.4

EC – electrical conductivity; OC – organic carbon

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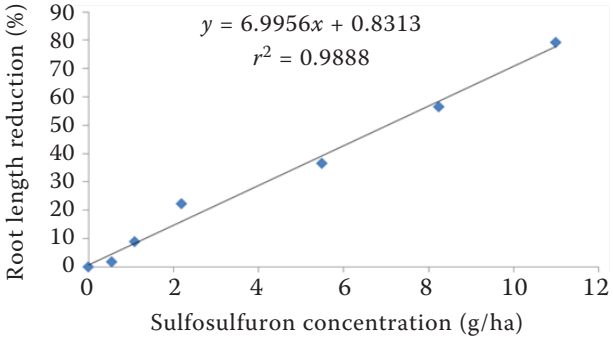

Figure 1. Root length reduction of garden cress by sulfosulfuron (26.6 g/ha)

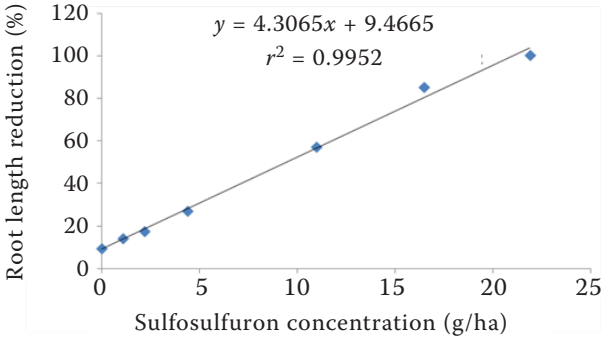

Figure 2. Root length reduction of garden cress by sulfosulfuron (53.2 g/ha)

Analysis of variance and comparison of means were performed using the least significant difference (*LSD*) test at $P \leq 0.05$ using SAS 9.1. (Cary, USA)

RESULTS

Herbicide residues by bioassay method. Sulfosulfuron residues at D1 in the first sampling in Y1 and Y2 were 10.75 and 10.40 µg/kg soil, respectively (Table 2). However, the amount of herbicide loss increased from 2.18% and 5.36% on the first day in Y1 and Y2 to 16.56% and 20.74% in the second sampling, respectively. The average residues of the herbicide in S6 in Y1 and Y2 were 2.42% and 1.81%, respectively (Table 2).

In general, the amount of herbicide residues was high at different intervals of sampling times in Y1. The herbicide residues were stable at D1 up to S7, at 1.41 and 0.52 µg/kg in Y1 and Y2, respectively. However, in S8 sulfosulfuron herbicide residues were not observed in the soil. According to the bioassay method, for D1 and D2 in Y1 and Y2, herbicide residues decreased, or herbicide loss increased (Tables 2 and 3).

The bioassay experiment also indicated that herbicide residues at D2 were stable up to S7 at 1.33 and 1.02 µg/kg soil (Table 3). Data obtained from

Table 2. Soil persistence of sulfosulfuron residues at the recommended rate (26.6 g/ha) by the bioassay method

Days[A]	Year	Root length[B] (cm)		Root inhibition (%)	Average residue (µg/kg)	Dissipation (%)
		untreated	treated			
0	1	11.3 ± 0.67	2.7 ± 0.34	76.1	10.75	2.18
	2	12.5 ± 1.3	3.3 ± 0.6	73.6	10.40	5.36
3	1	12.3 ± 0.48	4.2 ± 0.58	65.0	9.17	16.56
	2	11.8 ± 0.75	4.5 ± 0.30	61.8	8.71	20.74
10	1	10.5 ± 1.2	4.9 ± 0.54	53.3	7.50	31.75
	2	11.0 ± 1.0	5.9 ± 0.40	46.4	6.51	40.76
20	1	11.0 ± 0.25	6.1 ± 0.75	44.5	6.24	43.22
	2	11.2 ± 1.1	6.9 ± 0.64	38.4	5.37	51.13
30	1	10.8 ± 0.9	7.8 ± 0.4	27.8	3.85	64.96
	2	9.5 ± 1.2	7.3 ± 0.54	23.2	3.19	70.97
60	1	11.2 ± 0.45	9.2 ± 0.45	17.8	2.42	77.97
	2	10.4 ± 0.5	9.0 ± 0.3	13.5	1.81	83.53
90	1	11.2 ± 1.1	10.0 ± 0.65	10.7	1.41	87.17
	2	11.0 ± 1.0	10.5 ± 1.1	4.5	0.52	95.26
125	1	11.0 ± 0.70	11.2 ± 0.30	0	BDL	100
	2	12.2 ± 0.8	12.4 ± 0.4	0	BDL	100

[A]Days after herbicide application; [B]The average of root length for 20 plants and four replicates; SD – standard deviation; BDL – below detectable level (1 µg/kg)

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Table 3. Soil persistence of sulfosulfuron residues at the double rate (53.2 g/ha) by the bioassay method

Days[A]	Year	Root length[B] (cm)		Root inhibition (%)	Average residue (µg/kg)	Dissipation (%)
		untreated	treated			
0	1	12.5 ± 1.2	2.5 ± 0.34	80.0	16.37	25.52
	2	11.9 ± 1.0	2.0 ± 1.3	83.2	17.12	22.11
3	1	13.0 ± 0.8	3.2 ± 0.9	75.4	15.31	30.34
	2	12.3 ± 0.4	2.6 ± 0.3	78.9	16.12	26.66
10	1	11.6 ± 0.8	4.1 ± 0.7	64.6	12.80	41.76
	2	12.1 ± 1.2	4.0 ± 0.6	67.0	13.35	39.26
20	1	10.6 ± 0.7	5.2 ± 0.5	50.9	9.62	56.23
	2	11.7 ± 1.0	5.3 ± 0.64	54.7	10.50	52.22
30	1	12.6 ± 0.5	7.3 ± 0.4	42.1	7.57	65.55
	2	11.5 ± 1.0	6.2 ± 0.54	46.1	8.65	60.64
60	1	11.0 ± 0.8	8.2 ± 0.6	25.4	3.69	83.21
	2	12.6 ± 0.7	9.0 ± 1.0	28.5	4.41	79.93
90	1	11.8 ± 1.4	10.0 ± 0.8	15.2	1.33	93.94
	2	12.2 ± 0.6	10.5 ± 0.8	13.9	1.02	95.35
125	1	11.6 ± 0.5	11.7 ± 0.3	0	BDL	100
	2	12.6 ± 0.4	12.5 ± 0.5	0	BDL	100

[A]Days after herbicide application; [B]The average of root length for 20 plants and four replicates; SD – standard deviation; BDL – below detectable level (1 µg/kg)

the loss percentage of sulfosulfuron herbicide were fitted to a three-parameter sigmoid model (Figure 3) indicating X_0 (time required to lose 50% of herbicide) for D1 in Y1 and Y2 were approximately equal to 21 and 18 days, respectively (Table 4).

Herbicide residues by HPLC method. Analysis of soil samples by HPLC for the first day of D1 showed the herbicide residues of 9.7 and 9.0 µg/kg soil, for Y1 and Y2, respectively. However, the corresponding values for D2 were 18.8 and 19.6 µg/kg soil, respectively. Herbicide loss was high at D2 in comparison with D1 (Table 5). Accordingly, in S2 about 16% of herbicide (averaged for the two years) was lost. However, for S6, the corresponding values were 77% for D1 and 68% for D2. In Y1 and Y2, HPLC was not able to detect the possible herbicide residues at S7 for any treatment (Table 5). Fitting the loss pattern of herbicide to the sigmoid model (Figure 4) indicated DT_{50} (half-life = X_0) at D1 as 19 days (Table 6).

DISCUSSION

The present research was conducted to investigate the persistence of sulfosulfuron herbicide in the soil

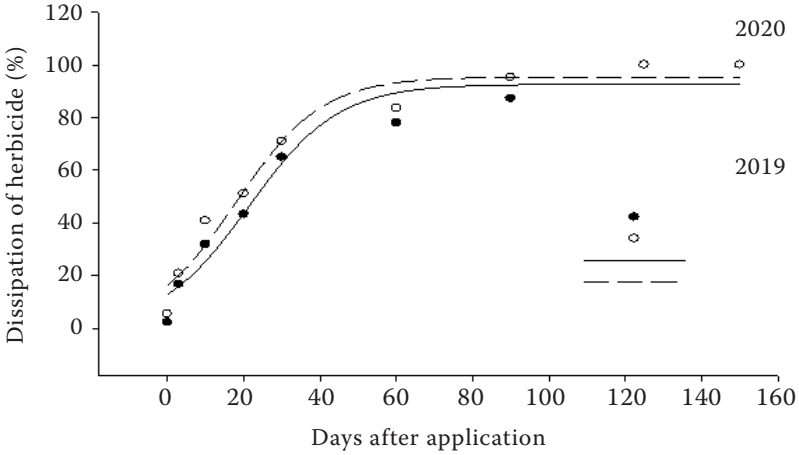

Figure 3. The pattern loss of sulfosulfuron herbicide at the recommended rate (26.6 g/ha) in 2019 and 2020 (bioassay method)

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Table 4. The three-parameter sigmoidal model $f = (a/(1 + exp\ (-(x - x_0)/b))$ to determine dissipation time (DT_{50}) of sulfosulfuron herbicide at the recommended rate (26.6 g/ha) by the bioassay technique

Model parameter	Year	
	1	2
A	92.66 (0.801)	94.46 (0.909)
B	11.68 (0.282)	11.27 (0.317)
X_0	21.32 (0.390)	17.84 (0.442)
R^2	0.97	0.98
RMSE	8.41	7.49
P-value	< 0.0001	< 0.0001

Values in parentheses indicate ± standard error; A – maximum dissipation of herbicide; B – the slope of the curve around X_0; X_0 – time required for 50% dissipation; R^2 – coefficient of determination; RMSE – root mean square error

Table 6. The three-parameter sigmoidal model $f = (a/(1 + \exp\ (-(x - x_0)/b))$ to determine dissipation time (DT_{50}) of sulfosulfuron herbicide at the recommended rate (26.6 g/ha) by the HPLC technique

Model parameter	Year	
	1	2
A	89.61 (0.92)	92.71 (0.94)
B	11.61 (0.24)	12.67 (0.27)
X_0	17.90 (01.14)	20.97 (01.25)
R^2	0.92	0.94
RMSE	9.17	9.73
P-value	< 0.0001	< 0.0001

Values in parentheses indicate ± standard error; A – maximum dissipation of herbicide; B – the slope of the curve around X_0; X_0 – time required for 50% dissipation; R^2 – coefficient of determination; RMSE – root mean square error

of wheat field. According to the HPLC and bioassay methods, the persistency of the herbicide was more than 90 days, however, at 125 days after use no residue was observed in the soil. Accordingly, a period of at least 125 days is essential for the complete decomposition of the herbicide in the soil. Such results are of environmental and health significance. The persistence of herbicide in the soil can affect the growth of the proceeding crop plants, and the environment including the surface and groundwater sources.

Our results are similar to the results of Paporisch et al. (2020), who found the residues of soil sulfo-

Table 5. Soil persistence of sulfosulfuron residues in wheat field soil at the recommended (26.6 g/ha) and double rates (53.2 g/ha) by the HPLC method

Time (days)	Year	Herbicide residue (± SD) (μg/kg)[A]	
		26.6 g/ha	53.2 g/ha
0	1	9.7 (± 0.031) [11.73]	18.8 (± 0.060) [14.46]
	2	9.0 (± 0.033) [18.10]	19.6 (± 0.054) [10.82]
3	1	9.4 (± 0.023) [14.46]	18.0 (± 0.073) [18.10]
	2	9.0 (± 0.021) [18.10]	18.8 (± 0.070) [14.46]
10	1	7.2 (± 0.032) [34.48]	NA
	2	8.1 (± 0.038) [26.29]	14.2 (± 0.067) [35.39]
20	1	5.0 (± 0.036) [54.50]	14.6 (± 0.055) [33.50]
	2	7.0 (± 0.026) [36.30]	11.6 (± 0.057) [47.22]
30	1	4.1 (± 0.029) [62.69]	12.0 (± 0.066) [53.19]
	2	3.0 (± 0.037) [72.70]	9.80 (± 0.051) [59.22]
60	1	2.6 (± 0.044) [76.34]	6.50 (± 0.075) [70.42]
	2	2.5 (± 0.047) [77.25]	7.50 (± 0.062) [65.67]
90	1	BDL	BDL
	2	BDL	BDL
125	1	BDL	BDL
	2	BDL	BDL

A – average of three replicates; numbers in square brackets indicate % dissipation; NA – not analysed; SD – standard deviation; BDL – below detectable level (1 μg/kg)

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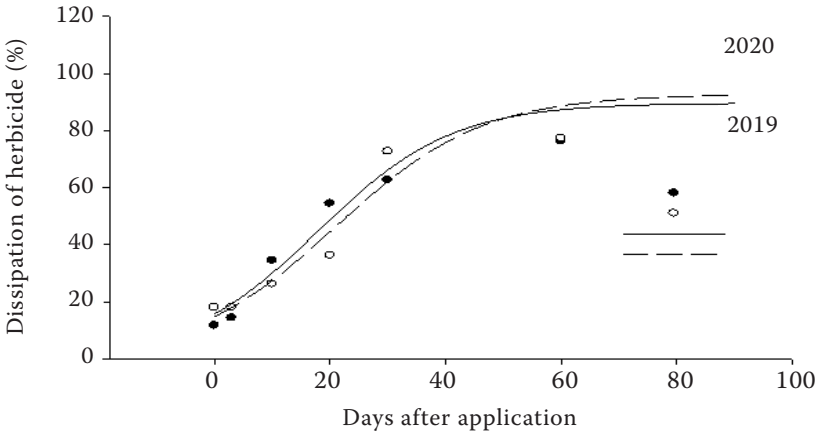

Figure 4. The pattern loss of sulfosulfuron herbicide at the recommended rate (26.6 g/ha) in 2019 and 2020 (HPLC method)

sulfuron decreased with time. Herbicide reduction is affected by many processes including absorption, decomposition, leaching and volatility depending on environmental conditions, agricultural practices, and physical and chemical properties of herbicides (Brillas 2021).

The two different methods indicated the higher sensitivity of the bioassay method for the detection of soil herbicide residues. According to the research, herbicide residues are strongly absorbed by colloidal particles over time so that the HPLC method is not able to detect the exact amount of residue. However, with time and while the plant is growing, the adsorbed herbicide residues gradually enter the liquid phase of the soil, and will be detected by the bioassay method compared with the HPLC method, indicating higher sensitivity of the bioassay method (Paul et al. 2009, Zhang et al. 2020).

According to the results it is possible to detect sulfosulfuron residues in the soil using HPLC (for a faster measurement) and bioassay (for a more precise measurement) methods. Depending on soil and climate properties, the time essential for decomposition of herbicide is different; however, according to our results, a minimum of 125 days may result in complete decomposition of herbicide. Such findings are of economic and environmental significance, as it they enable determining of the precise rate of herbicide for future applications.

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