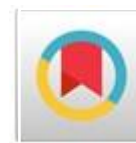




Dissipation of Glyphosate and Glufosinate Ammonium in Soil and Weed Control in Citrus Orchards



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Abstract: Glyphosate (GLY) and glufosinate-ammonium (GLUA) are broad-spectrum, non-selective, contact herbicides that are commonly used in fruit farms. Achieving the separation and detection of glyphosate and glufosinate from soil samples by chromatography is a challenging task as they are ionic and highly water-soluble compounds. The aim of this study is conducted to determine the dissipation of GLY and GLUA applied at two dose levels in three-depth soils of orange orchards. The residues of GLY and GLUA were determined by the HPLC-UV detector. The residual detection limits of GLY and GLUA of the method were 0.03 and 0.05 ng/g in soil respectively. The obtained data indicated that GLY persistent in the soil is very short, only for 7 days, following applications of 1 to 2 kg/fed in the orange crop. GLUA dissipated in soil within 14 days of application, regardless of dose. The half-life ($T/2$) of GLY and GLUA were 1.68 and 1.42 days at 0 cm depth, respectively. There was no significant difference between the half-life of the two herbicides in soil at three depths. These results showed that GLY dissipation occurs rapidly in soil. However, GLUA was moderately persistent in soil. The two compounds tested showed a reduction of dry weight for four types of weeds after 14 days of recommended and double-rate application.

1 Introduction

Glyphosate (N-(phosphonomethyl) glycine) is a non-selective herbicide widely used for the elimination of weeds in aquatic environments, for drying in no-till crops and among rows of perennial crops (Chamkasem and Harmon 2016). It is applied after emergence through aposymbiotic translocation. Target of glyphosate enzyme 5-enolpyruvylshikimate-3-phosphate synthase (EP-SPS) interfering with the biosynthesis of amino acids (Roberts et al 1998, Carretta et al 2021).

Glufosinate (2-amino-4-[hydroxyl (methyl) phosphor-yl]butanoic acid), also called phosphinothricin is used throughout the world to control a broad range of broadleaf weeds in fruit orchards, other crops and pre-emergence in vegetables (Royer et al 2000, Chamkasem and Harmon 2016). In soil, glufosinate-ammonium is primarily broken down to methyl phosphinico-propionic acid (MPP), which can be further degraded into 2-methylphosphinico-acetic acid. In general, GLY is not metabolized by plants and is therefore not selective. Only genetically modified varieties will be resistant consequently, virtually the

entire concentration of the active ingredient used hits the soil in its original state (Halim and Kuntom 2013, Nagatomi et al 2013 Janaki et al 2019). Soil degradation in the field indicates that GLUA is not very persistent (DT_{50lab} . Corr. 20°C = 6-11 days). The degradation half-life for GLUA in soil ranged from 2.30 to 2.93 days in a field (Zhang et al 2014). Bandana et al (2015), reported that the GLY is slowly degraded by microorganisms, it is highly adsorbed by soil and the half-life of GLY was between 5 to 19 days in tea field soil. The degree of degradation of GLY depends on the kind of microbial community found in soil because it degrades easily due to enzymes freed from microbes (Tu et al 2001). The phosphorous content in GLY is responsible for its microbial degradation. because micro-organisms require phosphorus to perform their metabolic functions (Lane et al 2012). Different methods were used in the analysis of glyphosate and glufosinate-ammonium. However, the unique physico-chemical characteristics of glyphosate make it difficult to determine residue concentrations, especially in soils with high levels of organic matter so two extraction methods have been used for the detection of glyphosate in soil using tandem mass spectrometry HPLC (De Gerónimo et al 2018). According to Ding et al (2015), glyphosate and its major metabolites were analyzed using gas or liquid chromatography combined with mass spectrometry. Zhang et al (2014), detected glufosinate residues in soil by GC-FPD (Flame Photometric Detector) after bypassing TMOA using a molten silica column.

The dissipation of GLY and GLUA at different depths and their effect on associated weeds are not investigated under Egyptian conditions on citrus fields. The objective of this study is to assess the degradation of GLY and GLUA after treatment at two rates at three depths of soil in orange orchards using HPLC.

2 Material and Method

A field experiment was carried out at the Farm of the Higher Institute for Agricultural Cooperation of Ain Shams University in 2019-2020. The experiment was structured into rows with three replicates per each sample. Commercial formulations of glyphosate (95% SG) and glufosinate-ammonium (20% SC) were purchased from SHOURA chemicals (Egypt) Herbicides were sprayed, using a mini sprayer hand Atomiz-

er, control weeds surrounding trees with two rates of application per herbicide 1 and 2 L/Fed for glyphosate while for glufosinate-ammonium 2 and 4 L/Fed.

2.1 Sampling of soil

Soil samples were randomly collected at approximately 0, 10 and 25 cm depth at successive intervals, i.e. 0, 3, 7, 14, 35 and 55 days after application. Samples were transferred directly to the laboratory into polyethylene bags and were stored at -20°C until the extraction.

2.2 Sample extraction, clean up and HPLC determination of tested herbicides

Glyphosate: The extraction was performed according to De Gerónimo et al (2018), with slight modifications. Briefly, 1 g soil sample was added to 5 ml of phosphoric acid: Water: methanol (1:1:8). The samples were kept overnight in the extraction solvent and then filtered using filter paper. The humidity was removed from the extract using anhydrous sodium sulfate which was placed on filter paper.

Glufosinate-ammonium: The test was performed according to Zhang et al (2014), with slight modifications. Briefly, 1 g soil sample was added to 5 ml of distilled water. The samples were afterward shaken using a mechanical shaker device for at least an hour, then filtered through filter paper (Whatman No1 H), then 5ml of acetone was added. The separating funnel was agitated vigorously for 3 min. The layer of solvent containing the residue of the herbicide was transferred to a separation funnel, then 10 ml methylene chloride was added and repeated at least 3 times. The extraction solvent was taken to dryness using a rotary evaporator set at 50-55°C. The extraction solvent layer was transferred to the solvent (petroleum ether) for the purification phase.

Cleanup: The extracts of both herbicides were cleaned up following the same procedure. A solid phase extraction (SPE) cleanup by using cartridge C18 was utilized as reported by Chamkasem and Harmon (2016). C18 cartridge was prepared with methanol follow-up water: methanol (50:50) containing 0.5 ml of sample extract and formic acid both separately, was loaded into the packed cartridge C18. The eluting solution of this conditioning step has been removed. In a second step, the sample extract (0.5 ml) was charged into cartridge C18 using eluted water: methanol containing formic acid, the same previous flows. The procedure was repeated 3 times. The elutes were collected

into around bottomed flask and then concentrated to dryness. The residues of both glyphosate and glufosinate were dissolved in 1 ml methanol and transferred in vials for HPLC.

2.3 Chromatographic conditions

The extracted samples (1 μL) were injected into the HPLC Agilent Technologies 1100 system under the following conditions: quaternary pump and UV detector. The mobile phase used for glyphosate was 25% methanol: 75% acetonitrile and for glufosinate-ammonium was 10% methyl acetate: 80% acetonitrile and 10% methanol. The mobile flow rate was 3 ml/min. C18: (25 cm length x 4.0 μg particles, x 4.6 mm internal diameters (i.d)).

2.4 Recovery study

The reliability of the analytical methods was tested with untreated samples containing known quantities of pesticides studied at concentrations of 0.1, 0.5 and 1 $\mu\text{g. gm}^{-1}$. The specimens were prepared according to the same extraction and cleaning procedures. The average recovery rates for glyphosate and glufosinate-ammonium were 93.38% and 91.71% in soil, respectively (Table 1). The observed concentrations of the obtained residues were corrected by the recovery rates.

Table 1. Percentage of recovery of glyphosate and glufosinate-ammonium in soil

Concentrations $\mu\text{g. gm}^{-1}$	Glyphosate	Glufosinate ammonium
1	94.66	92.261
0.5	92.972	91.62
0.1	92.515	90.26
Average	93.38	91.38

*Average of four replicates

2.5 Standard curve of glyphosate and glufosinate-ammonium

Series of graduated concentrations 0.4, 0.8, 1.2, 1.6, 2, 2.4, 2.8, 3.2, 3.6 and 4 μg (a.i.) gm^{-1} in acetonitrile was prepared and each concentration was injected under the previously mentioned conditions. The resulting peak area was plotted against $\mu\text{g gm}^{-1}$ of each concentration and a calibration curve was established. The obtained results are illustrated in Fig (1 and 2). The calibration curves demonstrated a correct linear relationship ($r^2 = 0.96$ and 0.98 respectively).

2.6 Efficiency of glyphosate and glufosinate against present weeds in citrus orchards

Herbicides phytotoxic effects of their recommended and double rate on citrus-associated weeds were tested through the following dry weight. Dry weight (mg) was recorded on 7 and 14 days using an electric balance after drying in an oven at 70°C for 48 h (Ashraf and Akhlaq 2007).

3 Results and Discussion

3.1 The dissipation of GLY residues in soil

The obtained data in Table 2, early deposits of GLY residues in the soil at 0 and 10 cm immediately after the application were found to be 1.563 and 0.99 $\mu\text{g/g}$; 3.17 and 1.36 $\mu\text{g/g}$ at 1 and two kg/fed application rates respectively. However, there is no detected residue at 25 cm depth. After 3 days GLY residues were determined as 0.454, 0.67 and 0.32 $\mu\text{g/g}$ in 0, 10 and 25 cm depth at 1 kg/fed rate of application.

Furthermore, glyphosate residues were found to be 0.094 and 0.49 $\mu\text{g/g}$, respectively in 0 and 10 cm depth at 2 kg/fed. doses of glyphosate application, but, not detected residue at 25 cm. Seven days after application, GLY dissipation was observed with low levels with 1 and 2.0 kg/fed application rates and the residues detected were 0.032 and 0.072; 0.043 and 0.081 $\mu\text{g/g}$ at 10 and 25 cm depth, respectively, with no detected residue at 0 cm. After the seventh day of application, the GLY level gradually dissipated until it could not be detected, except at 25 cm depth after 14 days it was recorded as 0.09 and 0.010 $\mu\text{g/g}$ which was degraded and no longer detected in the successive intervals.

These results are in harmony with (La Cecilia and Maggi 2018) who mentioned that glyphosate breaks down rapidly in soil, and it is completely degraded by soil micro-organisms. Glyphosate appeared to be directly and quickly degraded by microbes, even at high rates of application, without negatively affecting microbial activity, (Haney et al 2000). The amount of glyphosate was comparable with Tseng et al (2004), where GLY levels in clay, red soil and brown loam, medium loam were 0.91, 0.13; <0.14, 0.10 $\mu\text{g/g}$ at 42 days post- application.

3.2 The dissipation of GLUA residues in soil

The glufosinate residue has been detected as 2.56, 0.39 and 0.002 $\mu\text{g/g}$ at a depth of 0 cm on the 0th, 3rd and 7th day respectively when it was used with 2kg/fed; while it was 3.17, 0.57 and 0.004 $\mu\text{g/g}$ at depth 0 cm on 0th, 3rd and 7th day respectively when it was

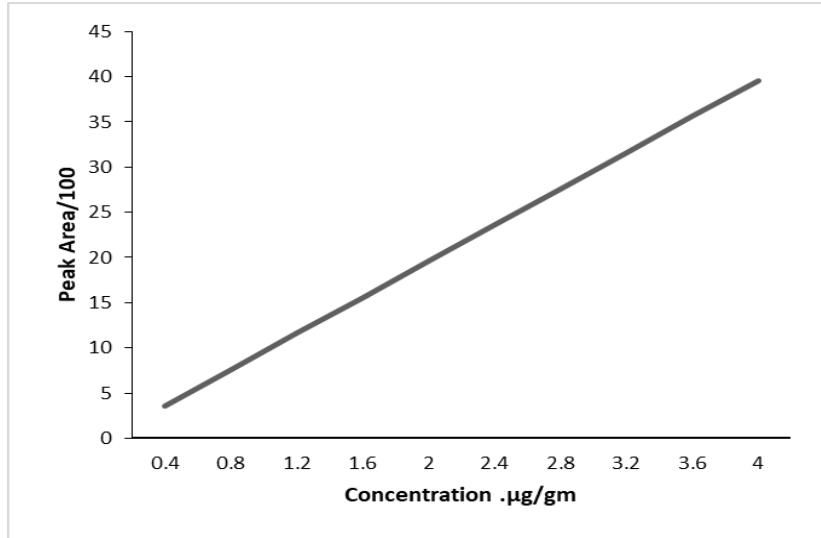


Fig 1. Standard curve of glyphosate

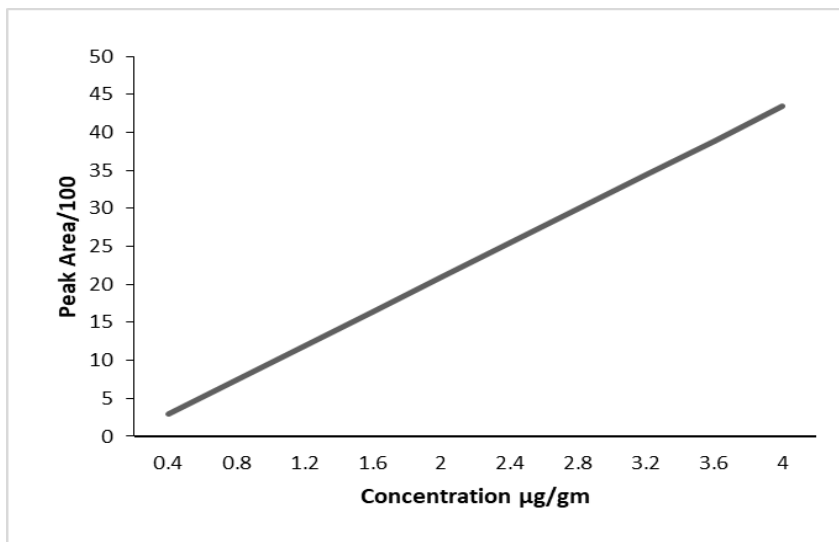


Fig 2. Standard curve of glufosinate ammonium

Table 2. Residues of glyphosate and % of dissipation in three levels of soil depth under field conditions

Sampling intervals (In days)	Detected residues(µg/g) and % of its dissipation at different depth of soil (0, 10, 25 cm)													
	(1 kg/fed.)						(2kg/ fed.)							
	0		10		25		0		10		25			
	R	D%	R	D%	R	D%	R	D%	R	D%	R	D%		
Zero time	1.563	—	0.994	—	ND	—	3.171	—	1.366	—	ND	—		
3	0.454	70.95	0.673	32.29	0.328	—	0.094	97.03	0.495	63.76	ND	—		
7	ND		0.032	96.78	0.072	78.04	ND		0.043	96.85	0.081	—		
14			ND		0.009	97.25			ND		ND		0.010	87.65
35					ND								ND	
55	ND		ND				ND		ND		ND			
Control					ND								ND	

R: Residues (µg/g soil)

D%: Percentage of dissipation

ND: Not detected below limit of detection (0.03 ng/g)

used with 2L/ fed 1.72,0.80 and 0.097, 1.92, 1.05 and 0.09 µg/g at depth 10 cm, 0, 0.10 and 0.037, 0, 0.20 and 0.06 µg/g at depth 25 cm in soil on 0th, 3rd and 7th day respectively, irrespective of the application rate (Table 3). The residues of glufosinate in soil declined progressively with time and on the 14th day it was below 0.024 µg/g except for 25cm on a double dose. The residues of the tested herbicides were not detected in all successive intervals of soil samples after 14 days of spraying in recommended and double doses in soil. Glufosinate ammonium was relatively moderately persistent in soil, this result agreement with the results by Janaki et al (2019) who reported that the initial residue in soil on 0, 15 cm depths was extended from 0.098 - 0.165 and 0.012 - 0.023 mg kg⁻¹, respectively, it was less than the residue after 30 days (0,011-0,017 mg kg⁻¹), irrespective of the application rate. A low concentration in soil at day 0 could occur because of the faster degradation mainly due to the microbial activity (Behrendt et al 1990).

3.3 Dissipation kinetic of glyphosate (GLY) and glufosinate-ammonium (GLUA) in soil

Degradation curves of herbicide residues over time were provided in Table 4. The charts show that the GLY and GLUA dissipate at 3 depths at two doses of application. A pseudo-first-order kinetic decay curve was observed at two doses. The coefficients, rate constants and regression equations are summarized in Table 4. Following application, the GLY concentration in treated soil was gradually reduced. The half-life (T/2) of Glyphosate was 0.56 days at 0 cm depth with a correlation coefficient of 1. There was no major difference in the half-life (T/2) of glyphosate in soil at 3 depths. Half-life (T/2) values for the

glufosinate ammonium at all three depths for two doses of applications (1 and 2 lit/fed) were found to be 0.25 and 0.27 days; 0.37 and 0.37 days; and 0.81 and 0.63 days, respectively. half-life (T/2) of GLUA was comparable to glyphosate at 3 depths. No significant half-life difference was observed for GLU at 3 depths. The highest tenth life period (T/10) for glyphosate at 10 cm for double the recommended rate (14.7 days). The maximum period of tenth life for glufosinate-ammonium was found to be 15.38 days at 25 cm for the recommended rate.

Glyphosate is highly adsorbed by soil, so degradation by microorganisms is rather rapid. It has a middle half-life in soil of two months (Tu et al 2001). In addition, the half-life for GLY averaged ranged from 5 to 19 days in tea field soil (Bandana et al 2015). Malik et al (1989), reported that glyphosate is moderately persistent in the field with a typical half-life in the field of 40 -60 days. The lower half-life values for this study can be attributable to the combined effect of the soil type.

Zhang et al (2014), reported that glufosinate ammonium gradually degrades to MPP and dissipates rapidly into the soil to MPA in a few hours. In addition, micro-organisms are the most significant factor affecting the degradation of GLUA in soil and leaving no residual activity. It was further degraded by micro-organisms and half-lives ranging from 1 to 25 days (Gallina and Stephenson 1992, Accinelli et al 2004). European Food Safety Authority EFSA (2005) stated that the persistence of GLUA in soil is attributed to the clay content rather than organic matter. According to the EPA (2005) the half-life of GLUA ranges from 8.5 to 23.0 days in soil based on the rate of application in aerobic soil. The calculated half-lives were 9.51 and 10.04 days, respectively, at the recommended dose (0.5 kg/ha) and twice the recommended dose (1.0 kg/ha) (Behrendt et al 1990).

Table 3. Residues of glufosinate ammonium and % of dissipation in three levels of soil depth under field conditions

Sampling intervals (In days)	Detected residues(µg/g) and % of its dissipation at different depths of soil (0, 10, 25 cm)											
	(2kg/ fed.)						2 Lit/ Fed.					
	0		10		25		0		10		25	
	R	D%	R	D%	R	D%	R	D%	R	D%	R	D%
Zero time	2.562	—	1.726	—	ND	—	3.176	—	1.928	—	ND	—
3	0.392	84.69	0.801	53.59	0.101	—	0.578	81.8	1.059	45.07	0.206	70.87
7	0.002	99.92	0.097	94.38	0.037	63.36	0.004	99.87	0.099	94.86	0.060	43.76
14	0.003	99.86	0.008	99.53	0.018	82.17	0.004	99.87	0.009	99.53	0.024	88.34
35	ND											
55												
Control												
	R: Residues (µg/g soil)						% D: Percentage of dissipation					

ND: Not detected below the limit of detection (0.05 ng/g)

Table 4. Degradation kinetics of glyphosate and glufosinate-ammonium residue in soil

Dose	Depths	Kinetic equation	Correlation coefficient (R ²)	Half-lives (T/2, days)	Half-lives (T/10, days)
Glyphosate 1 kg/fed.	0	$y = -0.53x + 3.66$	1.00	0.56	5.61
	10cm	$y = -0.75x + 3.88$	0.83	0.43	4.76
	25 cm	$y = 0.91x - 0.38$	0.50	0.33	7.14
Glyphosate 2 kg/fed.	0	$y = -1.52x + 4.96$	1.00	0.2	1.17
	10cm	$y = -0.26x + 2.76$	0.11	1.15	14.70
	25 cm	$y = 0.455x - 0.45$	0.44	0.66	3.70
Glufosinate Ammonium 1 lit/ fed	0	$y = -1.164x + 4.45$	0.84	0.25	4.76
	10cm	$y = -0.80x + 4.201$	0.95	0.37	5.88
	25 cm	$y = -0.3705x + 2.7845$	0.81	0.81	15.38
Glufosinate Ammonium 2 lit /fed	0	$y = -1.11x + 4.54$	0.88	0.27	4.41
	10cm	$y = -0.795x + 4.23$	0.95	0.37	10.24
	25 cm	$y = -0.475x + 3.17$	0.99	0.633	12.34

Examining the obtained results revealed that the rapid dissipation of glyphosate and glufosinate at the surface layer of soil could attributed to photo-degradation or volatilization process from soil, The Vapor Pressure of glyphosate and glufosinate are 9.8×10^{-8} mm Hg / 1.31×10^{-2} mPa/ at 25°C and 1.0×10^{-4} at 25°C, respectively (Tomlin 1997). Considering that the field experiments were carried out under high Sunlight Intensity. Furthermore, glyphosate and glufosinate-ammonium are ionic and highly water-soluble compounds, whereas, the partition coefficient (LogP) for glyphosate and glufosinate-ammonium are -3.4 (Sangster 1997) and < 0.1 (Lyman et al 1990, Tomlin 1997), which indicates the high polarity of these compounds. Such high solubility in water generates a rapid leaching in the soil column. Also, the effect of soil texture which contains highly coarse particles increases the rate of move-down mobility. As for the 10 and 25 cm depths, there was extreme rain after 20 days from the spraying period.

3.4 Efficiency of glyphosate and glufosinate-ammonium against present weeds

All tested herbicides significantly reduced the dry weight of all weeds (*Cynodon dactylon* L, *Convolvulus arvensis* L, *Sonchus oleraceus* L and *Sisymbrium irio* L) [Table 5 and 6]. The height reductions (100%) were observed of the double rate of glufosinate ammonium, except for, a reduction in Bermuda grass was showed of 99.89 % of dry weight. However, the highest % reduction

in dry weight was recorded against weeds after 7 days by the two tested herbicides especially, the recommended double rate.

Barbora et al (2002), and Singh et al (2011), indicated that glyphosate exhibited perfect weed control (annual and perennial grass and broadleaved) in different orchard crops such as citrus. GLY and GLUA were found to reduce weed biomass 28 days after treatment (Mohamed 2017). Following treatment and disruption of biochemical processes by glyphosate, plants begin to die. Annual plants begin to exhibit symptoms within two to four days, whereas perennials take seven to ten days. Wibawa et al (2009), reported that variables in response of weed species to glyphosate or glufosinate-ammonium may have attributed to the growth and dominance characteristics of weed groups such as density, frequency and productivity of weed community or it might contribute to the difference in the target site actions. Glyphosate is an inhibitor of the EPSPS, a key enzyme in the shikimate pathway which blocks the synthesis of the essential amino aromatic acids such as phenyl aniline and tryptophan causing accumulations of shikimate in the plant tissues and then plant death. In addition, glyphosate can deactivate the chlorophyll synthesis in plants causing yellowish leaves through an increase in chlorophyll content in plants (Cole 1985, Gravena et al 2012). Plants sensitive to ammonium glufosinate showed deficiency in glutamine poisoning by the accumulation of ammonia, glutamate, glyoxalate, fracture of the chloroplast structure and suppression of photosynthesis (Coetzer and Al-Khatib 2001, Carbonari et al 2016, Dayan et al 2015).

Table 5. Effect of glyphosate and glufosinate-ammonium on dry weight (D.W) of weeds under field conditions

Treatments	<i>Cynodon dactylon</i> L (Bermuda grass)				<i>Convolvulus arvensis</i> L (Field Bindweed)			
	Days after application							
	7		14		7		14	
	D.W.	% reduction	D.W.	% reduction	D.W.	% reduction	D.W.	% reduction
Glyphosate 1kg/fed.	0.46 ± 0.14b	76.04	0.02 ±0.03b	99.3	2.03 ±0.34bc	66.77	0.74 ±0.22b	88.7
	0.21 ± 0.15c	89.06	0.02 ±0.04b	99.3	2.14 ±0.38bc	64.97	0.26 ±0.46bc	96.03
Glufosinate ammonium 2 lit/ fed.	0.46 ± 0.25b	76.04	0.03 ±0.04b	98.95	2.37 ± 1.25b	61.21	0.20 ±0.36c	96.94
	0.02 ± 0.02c	98.95	0.003 ±0.01b	99.89	1.25 ± 0.35c	79.54	0 ±0c	100
Control	1.92 ± 0.30a		2.87 ±0.41a		6.11 ± 1.05a		6.55 ±0.56a	
LSD _{0.05}	0.18		4.12		0.66		0.34	

Table 6. Effect of glyphosate and glufosinate ammonium on dry weight (D.W) of weed under field conditions

Treatments	<i>Sonchus oleraceus</i> L (Annual Sow thistle)				<i>Sisymbrium irio</i> L (London Rocket)			
	Days After Application							
	7		14		7		14	
	D.W.	% reduction	D.W.	% reduction	D.W.	% reduction	D.W.	% reduction
Glyphosate 1kg/fed.	4.99 ±1.93b	82.17	0.04 ±0.13b	99.86	3.8 ± 1.50b	78.44	0.19 ±0.65b	98.98
	4.38 ±0.88b	84.35	0 ±0b	100	2.06± 0.09bc	88.31	0.12 ±0.43b	99.35
Glufosinate ammonium 2 lit/ fed.	4.86 ±0.41b	82.64	0.11 ±0.39b	99.63	4.86 ±1.05bc	72.43	0.09 ±0.32b	99.51
	4.33 ±1.13b	84.53	0 ±0b	100	4.33 ± 0.82c	75.43	0 ±0b	100
Control	28 ± 2.21a		29.86 ±1.55a		17.4 ± 3.21a		18.63 ±2.91a	
LSD _{0.05}	1.34		0.65		1.35		1.23	

4 Conclusion

Examining the obtained results, it is concluded that, the rapid dissipation of glyphosate and glufosinate at the surface layer of soil compared to 5, 20 cm depth was revealed. Glyphosate and glufosinate were dissipated in soil within 7 and 14 days of application, respectively, regardless of dose. Additionally, both tested pesticides showed significant herbicidal activity against the four examined weeds, particularly, after 14 days of application.

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