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Effects of adjuvants on the effectiveness and rainfastness of rimsulfuron in potato

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Abstract: Using adjuvants to optimize and increase the efficacy of herbicides is an acceptable manner to reduce herbicides undesirable impact on the environment in sustainable agriculture. In this study, it was demonstrated that the application of 0.1% of the non-ionic surfactant (NIS, Contact) and 0.5 L ha^{-1} of a crop oil concentrate (COC, Renol) did not improve the efficacy of rimsulfuron on *Amaranthus retroflexus.* In contrast, the same treatments enhanced performance and rainfastnes of rimsulfuron in *Chenopodium album* in pot expriments. Increasing non-ionic surfactant concentration to 1 L ha^{-1} increased rimsulfuron performance around 11-fold for *Amaranthus retroflexus* compared to around 3-fold for *Chenopodium album.* The same treatment, also reduced the rainfastness of rimsulfuron on *Amaranthus retroflexus* while improving the rainfastness of rimsulfuron on *Chenopodium album*. Measured ED_{50} and ED_{90} values of rimsulfuron indicated that the addition of the 0.2 L ha^{-1} of NIS improved the recommended (60 g ai. ha^{-1}) and the reduced (30 g ai. ha^{-1}) of rimsulfurom in field. The highest potato yield measured (60 tons per ha) when 60 g ai. ha^{-1} rimsulfuron was applied at three stages (S1, S4, and S7) without using a NIS; not significant differences were measured when the same dose of rimsulfuron was applied at the three (S1, S4, and S7) and two (S1, S4) stages with NIS.

Keywords: Chemical control; Dose-response; Herbicide efficacy; Growth stages; Surfactant

1. Introduction

Potato (*Solanum tuberosum* L.) is the fourth-largest crops in the world after wheat, rice and maize in terms of human consumption [1,2]. Weeds significantly reduce the tuber yield whereas weed control treatments substantially increase the tuber yield as well [3]. It is well documented that weed direct competition cause sever tuber yield reduction [4,5]. Weed competition had negative effects on potato crop expressed in reducing tuber yield by 32.7% [6] and up to 86% as well as tuber quality. The most important weeds in potato in Iran are *Amaranthus* spp., *Chenopodium album* L., *Portulaca oleracea* L., *Polygonum* spp., *Setaria* spp., *Echinochloa crus gali*, *Hordeum leporinum* and *Lolium* spp. [7]. Summer annual broadleaf weeds such as common lambsquarters (*Chenopodium album* L.) and redroot pigweed (*Amaranthus retroflexus* L.) are the most common and problematic weed species in temperate-season potato fields [8,9]. Metribuzin is a common selective herbicides in potato which is controlling vast range of species including broad and narrow leaves [10] except for *Solanum sarrachoides* (L.) [11]. Intensive use of metribuzin caused increasing number of resistant weeds [12,13]. The most important resistant weed species are *Solanum.*

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sarachoides (L.), *Solanum triflorum* [14], *Amaranthus retroflexus* [15], *Chenopodium album* [16], Raphanus raphanustrum [17] and *Lolium rigidum* [18]. Some potato cultivars, however, are not that tolerant to metribuzin. Rimsulfuron is a widely used post-emergence sulfonylurea herbicide with desirable properties such as high efficacy, broad-spectrum weed control and low toxicity to mammalian organisms. It inhibits acetolactate synthase (ALS), an important enzyme in the biosynthesis of branched-chain amino acids (leucine, isoleucine and valine) in plants [19]. Pre and Post emergence application of rimsulforun effectively controlled *C. album* and *A. retroflexus* that are important weeds in the crop [8,20,21]. The optimization of herbicide use allows for dose reductions [12].

It is generally accepted that the optimization of herbicide use allows for dose reductions. To optimize herbicide use aspects such as the best time of application [22] and appropriate use of adjuvants have to be investigated. An adjuvant is a biologically inert substance, but when added to herbicide herbicide spraying solutions, it could change the surface characteristics of herbicide droplets, affect the bioavailability of the herbicide molecules, and alter the diffusion coefficient of the herbicide molecule [23]. It enhance retention, coverage and efficacy of the applied herbicide [24]. Numerous types of adjuvants exist such as surfactants, oils, and fertilizers. Surfactants are classified as non-ionic, anionic, cationic or zwitterionic [13]. Rimsulfuron needs adjuvant to optimize its efficacy and rainfastness similarly to other ALS herbicides [25,26]. Previous studies reported that density, viscosity, surface tension, contact angle, droplet size, and droplet evaporation of the spray solution could change with the addition of adjuvants to the spray solution [27]. Therefore, improvement in the retention capacity of droplets could be an approach to increase the herbicide performance and to reduce its dosage [28]. The type and the concentration of the applied adjuvant influence rimsulfuron activity. As such, rimsulfuron applied at 4 different dosages (e.g. 9, 18, 26, or 35 g ha^{-1}), with a different types of adjuvants such as a nonionic surfactant (NIS), a crop oil concentrate (COC), a methylated seed oil (MSO), or an organosilicon surfactant (SIL), the mean common lambsquarters (*C. album*) control reached 75%, regardless of the type of adjuvant or rimsulfuron dose [20]. It should be noted NIS has been recommended to be used by rimsulfuron in post-emergence applications, previous researches suggested MSO and COC to improve efficacy of rimsulfuron [14]. Methylated seed oil (MSO) and NIS promote the foliar absorption and efficacy of rimsulfuron and several graminicides for grass weed control [29]. Herbicide applications carry the risk of reduced efficacy if rainfall occurs shortly after application. Activators (surfactants) change characteristic herbicides such as viscosity and particle size, evaporation, etc. They improved herbicide activity, and rainfastness [30] which is another reason to consider for selecting an adjuvant [31]. Rainfastness was defined as the time required after herbicide usage for adequate absorption to occur so that, herbicide activity not to be diminished by rainfall [32]. Although previous studies have shown that surfactants increased the performance [33] and decrease rainfastness of herbicides [34], an important question still arise whether each kind of surfactant will be compatible to increase efficacy of each kind of herbicide or not.

As far as, *Amaranthus retroflexus* and *Chenopodium album* are the two problematic weeds in potato [8], given the limited available herbicides for their control, it is important to investigate solutions for their effective control. The aim of this research was assessing of two types of surfactants (NIS and COC) in (i) improving rimsulfuron performance against *Chenopodium album* and *Amaranthus retroflexus,* (ii) minimizing rainfall adverse effect against rimsulfuron performance and (iii) evaluating of NIS surfactant in increasing rimsulfuron performance at reduced doses in potato field.

2. Materials and Methods

2.1. First outdoor pot experiment

The experiment was carried out in 2011 at the Department of Agroecology, the University of Aarhus, Denmark (55°19′N,11°23′E). The first and second experiments were

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done in pots that were placed outdoors. *Chenopodium album* and *Amaranthus retroflexus* seeds were obtained from the seedbank of the University of Aarhus, Denmark. Twenty seeds of *C. album* and *A. retroflexus* per pot were sown in 2 L plastic pots filled by an automatic seed sowing machine. The potting mixture included: sandy loam soil, sand, and peat (2:1:1 w/w/w respectively, 4.2% organic matter and a pH of 6.9). The pots were sub-irrigated five times a day by deionized water after seedling emergence, just four plants were kept in each pot. At four to six-leaf growth stages, plants were treated by the herbicide. Commercial rimsulfuron (Titus DF, 250 g kg^{-1}) were used in a laboratory pot sprayer equipped with two flat–fan nozzles (4110-14; Hardi; Taastrup, Denmark) working at 260 kpa and delivering 155.3 L ha^{-1}. Rimsulfuron was used singly and in a mixture of surfactants. The target weeds were *C.album* and *A.retroflexus* in a factorial experiment with three factors. Plants were subjected to without and with 5 mm rain at different times by a rain simulator which was working at an intensity of 9 mmh^{-1} [26]. The treatments used are shown in **Table 1.** The first factor was the different rimsulfuron doses (seven levels; such as 0, 1.872, 3.75, 7.5, 15, 30, 60 g ha^{-1}); the second factor was the type of surfactant (two levels; such as Contact {a non-ionic surfactant, 980 g/l linear alcohol ethoxylate, from Nufarm company (NIS), 0.1%}, Renol {a crop oil concentrate (COC), 0.5 L ha^{-1}} and the third factor was the time of 5 mm rain (four levels; such as 0, 1, 2, 4 hours after treatment (HAT) for *C. album* (**Table 1**). For *A. retroflexus*, the first factor was the different rimsulfuron doses (seven levels; such as 0, 0.2343, 0.468, 0.9375, 1.875, 3.75, 7.5 g ha^{-1}); the second factor was the type of surfactant (two levels; such as Contact (NIS, 0.1%), Renol (COC, 0.5 L ha^{-1}) and third factor was the time of 5 mm rain (four levels; such as 0, 1, 2, 4 hours after treatment (HAT). The pots were located on a table outdoor adopting a factorial experiment in the base of a completely randomized block design with three replications. Plants were harvested three weeks after herbicide application and fresh and dry weight were measured. Dry weight of experimental pots (all of the plants in each pot) oven-dried at 75 °C for 48 h and then weighed.

Table 1. The list of treatments for all the experiments that refer to rimsulfuron and surfactants doses; the first and second outdoor pot experiments and the two field experiments. NIS: non-ionic surfactant, COC: crop oil concentrate, and HAT: hours after treatment, the application timings (see Table 2) were as follows: i) S1: Leaf development; ii) S1+S4: leaf development (S1) + vegetatively propagated organs (S4); and iii) S1+S4+S7: leaf.

First outdoor pot experiment				
Species	**Rimsulfuron (g ha^{-1})**	**Contact (NIS)**	**Renol (COC)**	**Rain**
Chenopodium album	0, 1.875, 3.75, 7.5, 15, 30, 60	0.1%	0.5 L ha^{-1}	0, 1, 2 ,4 HAT
Amarathus retroflexus	0, 0.2343, 0.468, 0.9375, 1.875, 3.75, 7.5	0.1%	0.5 L ha^{-1}	0, 1, 2 ,4 HAT
Second outdoor pot experiment				
Species	**Rimsulfuron (g ha^{-1})**	**Contact (NIS)**	**Renol (COC)**	**Rain**
Chenopodium album	0, 1.875, 3.75, 7.5, 15, 30, 60	0.04. 0.2, 1 L ha^{-1}	-	0, 1, 2 ,4 HAT
Amarathus retroflexus	0, 0.2343, 0.468, 0.9375, 1.875, 3.75, 7.5	0.04. 0.2, 1 L ha^{-1}	-	0, 1, 2 ,4 HAT
Field experiment (Reduced dose)				
Species	**Rimsulfuron (g ai. ha^{-1})**	**Contact (NIS)**	**Renol (COC)**	**Application time**
Chenopodium album	0, 5, 10, 15, 20, 25, 30	0.2 L ha^{-1}	-	S1, S1+S4, S1+S4+S7
Amarathus retroflexus	0, 5, 10, 15, 20, 25, 30	0.2 L ha^{-1}	-	S1, S1+S4, S1+S4+S7
Field experiment (Recommended dose)				
Species	**Rimsulfuron (g ai. ha^{-1})**	**Contact (NIS)**	**Renol (COC)**	**Application time**
Chenopodium album	0, 10, 20, 30, 40, 50, 60	0.2 L ha^{-1}	-	S1, S1+S4, S1+S4+S7
Amarathus retroflexus	0, 10, 20, 30, 40, 50, 60	0.2 L ha^{-1}	-	S1, S1+S4, S1+S4+S7

2.2. Second outdoor pot experiment

 doi:10.20944/preprints202305.2124.v1

The treatments used are shown in **Table 1**. In this experiment, plants of *C. album* and *A. retroflexus* were sprayed with the same rimsulfuron doses and exposed to the same rain treatments, as in the 1st outdoor pot experiment. The NIS (Contact) was used in 0, 0.04, 0.2, and 1 L ha^{-1} for *C. album* and *A. retroflexus*. Plants were harvested three weeks after herbicide application and fresh and dry weight were measured. Dry weight of experimental pots (all of the plants in each pot) oven-dried at 75 °C for 48 h and then weighed.

2.3. Field experiments

Two field experiments were performed at Sheikh Kalkhoran of Ardabil (48° 20′ N, 38° 15′ E) in Iran, on a loam soil (42% sand, 32% silt, and 26% clay), in 2015. Soil organic matter and pH were 0.9% and 7.68, respectively. Fertilizers applied according to soil test recommendations which were used by irrigation systems during the growing season. Seed potatoes (cv. Agria) were planted 10 cm deep at 25 cm distances in rows separated 75 cm apart from each other on April 21, 2015, after soil tillage on October 13, 2014. Plots were sprayed against insects and diseases as needed and irrigated during the growing season with overhead sprinklers to obtain 65% minimum soil water content. Two experiments were planned in a factorial experiment in the base of a complete randomized block design with three replications with a plot size of 2*4 m^2. The treatments of field experiments with the reduced and recommended dose used were shown in **Table 1**. There were three factors on *C. album* and *A. retroflexus* in field experiments with a reduced dose. The first factor was rimsulfuron reduced doses (0, 5, 10, 15, 20, 25, 30 g ai. ha^{-1}), the second factor was Contact surfactant doses (0 and 0.2 L ha^{-1}) and the third factor was the time of application (S1, S1+S4, S1+ S4+S7) on *C. album* and *A. retroflexus* (**Table 1**). For a recommended dose of rimsulfuron in field experiments, the first factor was rimsulfuron recommended doses (0, 10, 20, 30, 40, 50, and 60 g ai. ha^{-1}), the second factor was Contact surfactant doses (0 and 0.2 L ha^{-1}) and the third factor was a time of application (S1, S1+S4, S1+ S4+S7) on *C. album* and *A. retroflexus* (**Table 1**). In both experiments, rimsulfuron was applied at leaf development (S1, one stage), leaf development (S1) + vegetatively propagated organs (S4) (two stages), and leaf development (S1) + vegetatively propagated organs (S4) + Development of tuber (S7) (three stages) [35] (**Table 2**). Commercial rimsulfuron (Titus DF, 250 g kg^{-1}) was applied by using a back-pack sprayer equipped with two flat–fan nozzles (8001; Inter) worked at 260 kpa and delivering 250 L ha^{-1}. Weed control was evaluated by harvesting weed plants within a quadrat of (0.75× 0.50 m^2) at three weeks after treatment. Three weeks after herbicide application, all of the plants in each plot were harvested and dried in an oven at 75 °C for 48 h then weighed. For determination of total tuber yield per hectare, center rows tuber of each plot were harvested and weighted.

2.4. Statistical Analyses

The dose-response data were analyzed using the R [36] program (Version 4.0.1) with the drc package (Version 4.0.1). The log-logistic regression of dry weight of *C.album* and *A. retroflexus* on dose was fitted with a log-logistic regression using a three parameters log-logistic model [37]:

$$y = \frac{d}{1 + \exp\left(b(\log(z) - \log(ED50)\right)} \tag{1}$$

where y is dry weight z, d is the upper limit where the dose is zero, ED_{50} denotes the dose required for reducing dry weight by half, and bis proportional to the slopes of the curves around ED_{50}. The ED_{50} parameter in Eq. (1) can be replaced by any ED level [38], (e.g., ED_{10}, ED_{90}).

The relative potency (RP) is the horizontal displacement between two curves at a chosen ED_x [31]. The biological exchange rate in a single application, i.e. the relative potency between the herbicides was calculated as follows:

$$\mathrm{RP} = ED_{50xf} / EDC_{50xf+v} \tag{2}$$

Where, ED_{xf} = the ED_x of herbicide alone; and ED_{xf+v}= the ED_x of herbicide in mixture with a surfactant. If RP = 1, the addition of surfactant does not affect herbicide performance. If RP was significantly higher or lower than 1, the herbicide in the mixture with the surfactant was more or less potent than the herbicide alone, respectively. Similarly, the rainfastness can be assessed by calculating the ratio between the ED_x dose with rain and the corresponding ED_x dose without rain.

Statistical analyses of yield data were performed using SAS (9.1) software. An ANOVA was performed using PROC GLM (PC-SAS) and when the F Test indicated significant effects, means were compared using LSD Fisher ($P < 0.05$) test.

Table 2. Principal potato growth stages that are related to the application timings in the field experiments.

Stage	Description
0	Germination / sprouting / bud development
1	Leaf development (main shoot)
2	Formation of side shoots / tillering
3	Stem elongation or rosette growth/shoot development (main shoot)
4	Development of harvestable vegetative plant parts or vegetatively propagated organs/booting (main shoot)
5	Inflorescence emergence (main shoot) / heading
6	Flowering (main shoot)
7	Development of fruit
8	Ripening or maturity of fruit and seed
9	Senescence, beginning of dormancy

3. Results

3.1. First outdoor pot experiment

Regarding the efficacy, the results showed no significant improvement on rimsulfuron performance due to both 0.1% NIS and 0.5 COC addition, on *A. retroflexus* (compare ED_{50} values of the 'no rain' treatments) (**Table 3**). In contrast, the inclusion of the 0.1% NIS adjuvant significantly improved the performance of rimsulfuron in *C. album* (**Table 3**). Regarding the rainfastness, 0.1% NIS and 0.5 COC improved rainfastness of rimsulfuron in *C. album* (**Table 3**). In *C. album*, the ED_{50} doses were much higher in comparison with to *A. retroflexus* and the non-ionic surfactant strongly improved the efficacy of rimsulfuron and had a strong effect on rainfastness while no significant impact of rain with Renol was shown except 4 HAT (**Table 3**). Also, the result showed that rainfastness was low without adjuvant and with 0.5 L ha^{-1} COC, but the inclusion of 0.1% NIS significantly improved the rainfastness, however full rainfastness of rimsulfuron was obtained only after 4 hours in *A. retroflexus* (**Table 3**).

Table 3. The effect of NIS and COC adjuvants on the effectiveness and rainfastness of rimsulfuron [applied at various timings: 1, 2, 4 HAT (hours after treatment)] on *Amaranthus retroflexus* and *Chenopodium album.* Relative rainfastness is the necessary length of a rain-free period following a herbicide application. The difference between ED_{50} data is based on the standard error with the letters for each species.

Amaranthus retroflexus				
Adjuvant	Rain	ED_{50} (g ha^{-1})	Confidence intervals	Relative rainfastness
None	No rain	0.28^{abc}	0.201-0.368	1.00
	1 HAT	4.68^{ijk}	3.318-6.036	16.71
	2 HAT	1.59^{fgh}	1.069-2.103	5.68
	4 HAT	1.34^{f}	0.937-1.743	4.79
0.1 % NIS	No rain	0.26^{ab}	0.182-0.345	1.00

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	1 HAT	0.55[de]	0.372-0.732	2.12
	2 HAT	0.51[d]	0.363-0.657	1.96
	4 HAT	0.28[abc]	0.184-0.382	1.08
0.5 L ha^{-1} COC	No rain	0.25[a]	0.179-0.330	1.00
	1 HAT	3.76[ij]	2.294-5.235	15.04
	2 HAT	3.74[i]	2.407-5.064	14.96
	4 HAT	1.44[fg]	0.910-1.970	5.76
		Chenopodium album		
None	No rain	26.47[e-i]	-14.78-67.72	1.00
	1 HAT	24.56[e-h]	6.13-42.98	0.93
	2 HAT	27.34[e-k]	-3.60-58.29	1.03
	4 HAT	31.16[e-l]	6.55-55.77	1.18
0.1 % NIS	No rain	1.89[a]	1.11-2.69	1.00
	1 HAT	4.18[d]	1.60-6.77	2.20
	2 HAT	2.06[ab]	0.85-3.28	1.08
	4 HAT	2.36[abc]	0.92-3.80	1.24
0.5 L ha^{-1} COC	No rain	13.28[e]	1.60-24.96	1.00
	1 HAT	21.44[efg]	5.09-37.79	1.61
	2 HAT	26.58[e-j]	3.39-49.77	2.00
	4 HAT	16.69[e-i]	-2.26-35.65	1.26

3.2. Second outdoor pot experiment

In the second experiment, the result showed that increasing the concentration of the NIS up to 1 L ha^{-1} improved the performance of rimsulfuron (**Table 4**). At 1 L ha^{-1}, regarding the efficacy, surfactant increased rimsulfuron performance around 11-fold compared to rimsulfuron 0.04 l ha^{-1} on *A. retroflexus*. On the contrary, increasing the concentration of the NIS sharply improved the performance of rimsulfuron on *C. album* (**Table 4**). Herbicidal performance was slightly more enhanced as concentration increased from 0.04 to 1 L ha^{-1}. At 1 L ha^{-1}, surfactant increase rimsulfuron performance around 3-fold compared to rimsulfuron 0.04 l ha^{-1} on *C. album* which was less compared to *A. retroflexus* (**Table 4**).

Increasing concentration of the NIS improved the rainfastness of rimsulfuron on *C. album*. Regarding to herbicidal performanc, the NIS is less efficient on *C. album* compared to *A. retroflexus*, but when tested for rainfasness showed more activity especially at 1 L ha^{-1} for *C. album* (**Table 4**). Each species had some distinct differences to the single surfactant properties. The spray deposit on the leaf surface is strongly related to cuticular structure and the adjuvant chemical tendency for retention on the leaf. Thus, the appropriate surfactant type and concentration increased rimsulfuron efficient. NIS efficacy was much higher compared to Renol. A surfactant concentration of 1 L ha^{-1} was required for maximum herbicidal performance, but regarding to rainfastness the results was different up to weed species.

Table 4. The effect of NIS adjuvant doses on the effectiveness and rainfastness of rimsulfuron [applied at various timings: 1, 2, 4 HAT (hours after treatment)] on *Amaranthus retroflexus* and *Chenopodium album.* Relative rainfastness is the necessary length of a rain-free period following a herbicide application. The difference between ED_{50} data is based on the standard error with the letters for each species.

		Amaranthus retroflexus		
Adjuvant	**Rain**	**ED_{50} (g ha^{-1})**	**Confidence intervals**	**Relative rainfastness**
0.04 L ha^{-1} NIS	No rain	0.33[cd]	0.219-0.437	1.00
	1 HAT	0.96[ij]	0.701-1.219	2.38
	2 HAT	0.59[fg]	0.433-0.757	1.49
	4 HAT	0.43[de]	0.302-0.553	1.16

0.2 L ha^{-1} NIS	No rain	0.12^{b}	0.051-0.196	1.00
	1 HAT	1.10^{jk}	0.789-1.406	4.22
	2 HAT	0.47^{def}	0.305-0.640	2.30
	4 HAT	0.43^{de}	0.306-0.559	1.73
1 L ha^{-1} NIS	No rain	0.03^{a}	-0.006-0.069	1.00
	1 HAT	0.73^{hi}	0.513-0.939	24.3
	2 HAT	0.70^{gh}	0.523-0.878	23.3
	4 HAT	0.29^{c}	0.191-0.396	9.67
		Chenopodium album		
0.04 L ha^{-1} NIS	No rain	5.37^{b-f}	1.44-9.30	1.00
	1 HAT	23.38^{ij}	7.89-38.86	4.35
	2 HAT	23.91^{jk}	1.62-46.21	4.45
	4 HAT	13.47^{e-i}	6.15-20.79	2.51
0.2 L ha^{-1} NIS	No rain	3.66^{a-d}	2.26-5.05	1.00
	1 HAT	9.86^{d-h}	4.50-15.21	2.69
	2 HAT	6.61^{b-g}	3.39-9.83	1.81
	4 HAT	5.17^{a-f}	2.71-7.62	1.41
1 L ha^{-1} NIS	No rain	1.75^{a}	0.84-2.66	1.00
	1 HAT	4.20^{a-e}	2.24-6.16	2.40
	2 HAT	2.97^{abc}	1.46-4.47	1.70
	4 HAT	2.38^{ab}	1.21-3.56	1.36

3.3. Field experiments

The results showed that increasing the doses of rimsulforun up to 60 g ai. ha^{-1} increased control of both *C. album* and *A. retroflexus.* The assessment three weeks after treatment demonstrate that rimsulforun at 40, 50, and 60 g ai. ha^{-1} in two (S1+S4) and three (S1+S4+S7) stages application provided 100% control of *C. album* and *A. retroflexus* (**Fig. 1, 2**). Application of rimsulforun at 25 and 30 g ai. ha^{-1} (e.g. 0.25X and 0.50X of the recommended dose) applied at the three stages (S1+S4+S7) provided full control of both weed species (**Fig. 1, 2**). When rimsulforun was combined with 0.2 L ha^{-1} NIS, *C. album* and *A. retroflexus* control was only slightly increased.

Tables 5 and **6** show the ED_{50} of the rimsulfuron applied singly and combined surfactant taken at various times of potato stages. The curves' upper limits were different for various doses and application time for each species, in some cases, the curves were crossing. The parameters ED_{10}, ED_{50}, ED_{90}, and *b* were estimated at each application time by fitting Eq. (1) for the *C. album*, and *A. retroflexus* biomass reduction. The ED_{50} values of rimsulforun were significantly reduced in two and three times of *A. retroflexus* at reduced dose of rimsulfuron. For *A. retroflexus*, the ED_{50} values of the reduced doses rimsulforun experiment (applied at one, two, three stages without surfactant), were 10.88, 6.37 and 3.09 g ai ha^{-1} vs. 7.27, 3.77 and 2.03 g ai ha^{-1} (applied at one, two, three stages with 0.2 L ha^{-1} NIS) (**Table 5**).

The reduced dose-response curves described the response well. The ranking of ED_{50} at reduced doses for the three application times was S1>S1+S4>S1+S4+S7 with and without surfactant (**Table 5**). Based on the ED_{50} values given in **Table 5** surfactants can improve the efficiency of rimsulfuron at reduced doses compared to rimsulforun alone. The ED_{50} values of rimsulforun were estimated based on *C. album* at reduced doses and one, two, three stages without surfactant 18.11, 12.31, 7.81 g ai. ha^{-1} and combined with surfactant 15.46, 10.66, 7.19 g ai. ha^{-1} on *C. album* (**Table 6**). The ED_{50} values at reduced doses and various time of application for *C. album* was higher than *A. retroflexus*. **Table 6** showed the same ED_{50} ranking of the potency of the three application time at the recommended dose of the *C. album* and *A. retroflexus* dose-response curves. The results of rimsulfuron on *C. album* dry weight showed that surfactant could not improve the efficacy of recommended

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dose of rimsulfuron at S1+S4 and S1+S4+S7. The estimated ED_{50} doses demonstrated that a reduced dose of rimsulfuron at S1+S4 and S1+S4+S7 provided full control of two species at 30 g ai. ha^{-1}. The relative potency (RP) values were different when NIS were added to this herbicide. RP values showed that surfactants can improve the efficacy of reduced and recommended doses of rimsulfuron for *A. retroflexus* at all application times and reduced doses at all application time and recommended doses at S1 stage.

Figure 2 showed that the highest potato yield measured (60 tons per ha) when 60 g ai. ha^{-1} rimsulfuron was applied at three stages (S1, S4, and S7) without using a NIS; not significant differences were measured when the same dose of rimsulfuron was applied at the three (S1, S4, and S7) and two (S1, S4) stages with NIS.

Table 5. The estimated regression parameters of the reduced rimsulfuron dose (1X: 30 g a.i. ha^{-1}), applied with and without NIS surfactant (1L ha^{-1}) on *Amaranthus retroflexus* L. and *Chenopodium album* dry weight at three different cropping times. The application timings (see Table 2) were as follows: i) S1: Leaf development; ii) S1+S4: leaf development (S1) + vegetatively propagated organs (S4); and iii) S1+S4+S7: leaf development (S1) + vegetatively propagated organs (S4) + Development of tuber (S7). The response variable is 0-100-percent weed control (dry weight reduction). The Relative potency (Rp) is explained in section 2.4. The difference between ED_{50} data is based on the standard error with the letters for each species.

Reduced dose without surfactant of *Amaranthus retroflexus* dry weight						
Application time	**slope**	**upper**	**ED_{10}**	**ED_{50}**	**ED_{90}**	**Rp**
S1	-6.04± 0.33	97.46 ± 0.78	7.56 ± 0.14	10.88 ± 0.09^{f}	15.64 ± 0.38	1.49
S1+S4	-5.48 ± 0.27	99.58 ± 0.59	4.27 ± 0.07	6.37 ± 0.09^{d}	9.52 ± 0.29	1.68
S1+S4+S7	-3.07 ±0.76	100.29 ± 0.73	1.51 ± 0.44	3.09 ± 0.35^{b}	6.32 ± 0.43	1.52
Reduced dose with surfactant of *Amaranthus retroflexus* dry weight						
S1	-4.09 ± 0.13	97.94 ± 0.33	5.93 ± 0.09	7.27 ± 0.07^{e}	12.60 ± 0.16	1.00
S1+S4	-2.69 ± 0.14	100.49 ± 0.39	2.77 ± 0.08	3.77 ± 0.06^{c}	8.70 ± 0.28	1.00
S1+S4+S7	-2.38 ± 0.45	100.36 ± 0.42	1.43 ± 0.33	2.03 ± 0.33^{a}	5.22 ± 0.15	1.00
Reduced dose without surfactant of *Chenopodium album* dry weight						
S1	-5.40 ± 0.47	79.05 ± 2.86	12.06 ± 0.32	18.11 ± 0.40^{f}	27.20 ± 1.46	1.17
S1+S4	-3.00 ± 0.18	104.00 ± 2.66	5.92 ± 0.20	12.31 ± 0.34^{d}	25.59 ± 1.72	1.13
S1+S4+S7	-3.37 ± 0.18	100.64 ± 1.21	4.07 ± 0.15	7.81 ± 0.16^{b}	15.00 ± 0.68	1.08
Reduced dose with surfactant of *Chenopodium album* dry weight						
S1	-4.41 ± 0.58	79.74 ± 3.90	9.51 ± 0.47	15.46 ± 0.58^{e}	25.73 ± 2.43	1.00
S1+S4	-2.97 ± 0.27	100.36 ± 3.32	5.09 ± 0.27	10.66 ± 0.43^{c}	22.31 ± 2.22	1.00
S1+S4+S7	-2.71 ± 0.23	102.67 ± 2.15	3.19 ± 0.21	7.19 ± 0.25^{a}	16.17 ± 1.44	1.00

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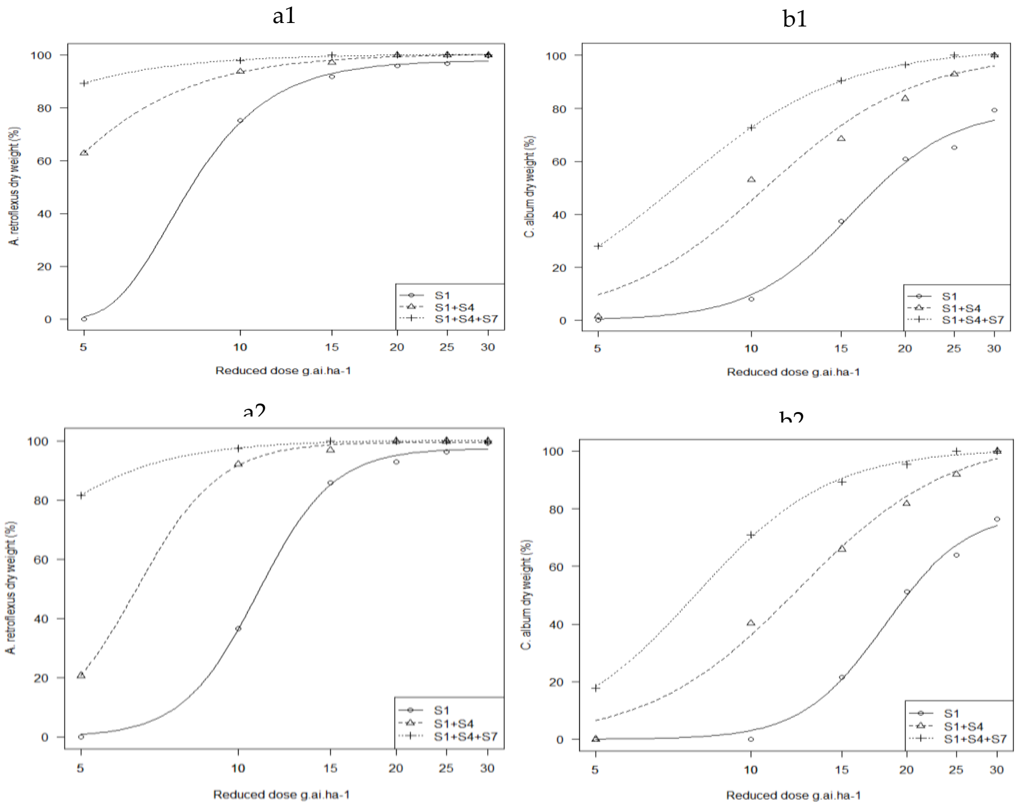

Figure 1. The effect of rimsulfuron application at a reduced dose (1X: 30 g a.i. ha^{-1}) without (1) and with (2) NIS surfactant (0.2 L ha-1) when applied at three cropping timings, on *Amaranthus retroflexus* (a) and *Chenopodium album* (b) dry weight. The application timings (see Table 2) were as follows: i) S1: Leaf development; ii) S1+S4: leaf development (S1) + vegetatively propagated organs (S4); and iii) S1+S4+S7: leaf development (S1) + vegetatively propagated organs (S4) + Development of tuber (S7).

Table 6. The estimated regression parameters of the recommended rimsulfuron dose (1X: 60 g a.i. ha^{-1}), applied with and without NIS surfactant (1 L ha^{-1}) on *Amaranthus retroflexus* L. and *Chenopodium album* dry weight at three different cropping times. The application timings (see Table 2) were as follows: i) S1: Leaf development; ii) S1+S4: leaf development (S1) + vegetatively propagated organs (S4); and iii) S1+S4+S7: leaf development (S1) + vegetatively propagated organs (S4) + Development of tuber (S7). The response variable is 0-100-percent weed control (dry weight reduction). The Relative potency (Rp) is explained in section 2.4. The difference between ED_{50} data is based on the standard error with the letters for each species.

Application time	Recommended dose without surfactant of *Amaranthus retroflexus* dry weight					
	slope	upper	ED_{10}	ED_{50}	ED_{90}	Rp
S1	-4.32 ± 0.25	100.19 ± 0.44	6.28 ± 0.17	10.41 ± 0.07^{a}	17.27 ± 0.55	1.63
S1+S2	-6.18 ± 8.04	100.02 ± 0.37	4.67 ± 4.61	6.67 ± 3.49^{a}	9.51 ± 0.61	2.07
S1+S2+S3	-6.73 ± 49.78	100.00 ± 0.36	3.87 ± 27.11	5.37 ± 24.61^{a}	7.44 ± 16.14	1.14
Recommended dose with surfactant of *Amaranthus retroflexus* dry weight						
S1	-2.60 ± 0.33	100.68 ± 0.64	2.73 ± 0.44	6.35 ± 0.36^{a}	14.76 ± 0.85	1.00
S1+S2	-2.37 ± 1.25	100.21 ± 0.68	1.27 ± 1.36	3.21 ± 1.86^{a}	8.11 ± 0.87	1.00
S1+S2+S3	-6.00 ± 43.54	100.00 ± 0.39	3.24 ± 26.42	4.67 ± 25.69^{a}	6.74 ± 19.15	1.00
Recommended dose without surfactant of *Chenopodium album* dry weight						
S1	-4.04 ± 0.35	94.93 ± 1.68	11.06 ± 0.49	19.05 ± 0.42^{a}	32.81 ± 1.96	1.08
S1+S2	-2.85 ± 0.23	102.37 ± 1.43	5.30 ± 0.34	11.44 ± 0.30^{a}	24.68 ± 1.83	0.88
S1+S2+S3	-3.10 ± 0.87	100.43 ± 1.27	3.54 ± 1.02	7.18 ± 0.67^{a}	14.57 ± 1.71	0.83
Recommended dose with surfactant of *Chenopodium album* dry weight						

S1	-3.27 ± 0.51	98.69 ± 3.53	9.02 ± 0.97	17.62± 0.92[a]	3.44 ± 4.31	1.00
S1+S2	-0.24 ± 0.25	170.19 ± 145.92	0.001 ± 0.005	12.86 ± 89.96[a]	9.79 ± 1.56	1.00
S1+S2+S3	-7.19 ± 26.69	100.00 ± 2.00	6.32 ± 10.72	8.58 ± 4.82[a]	1.16 ± 6.68	1.00

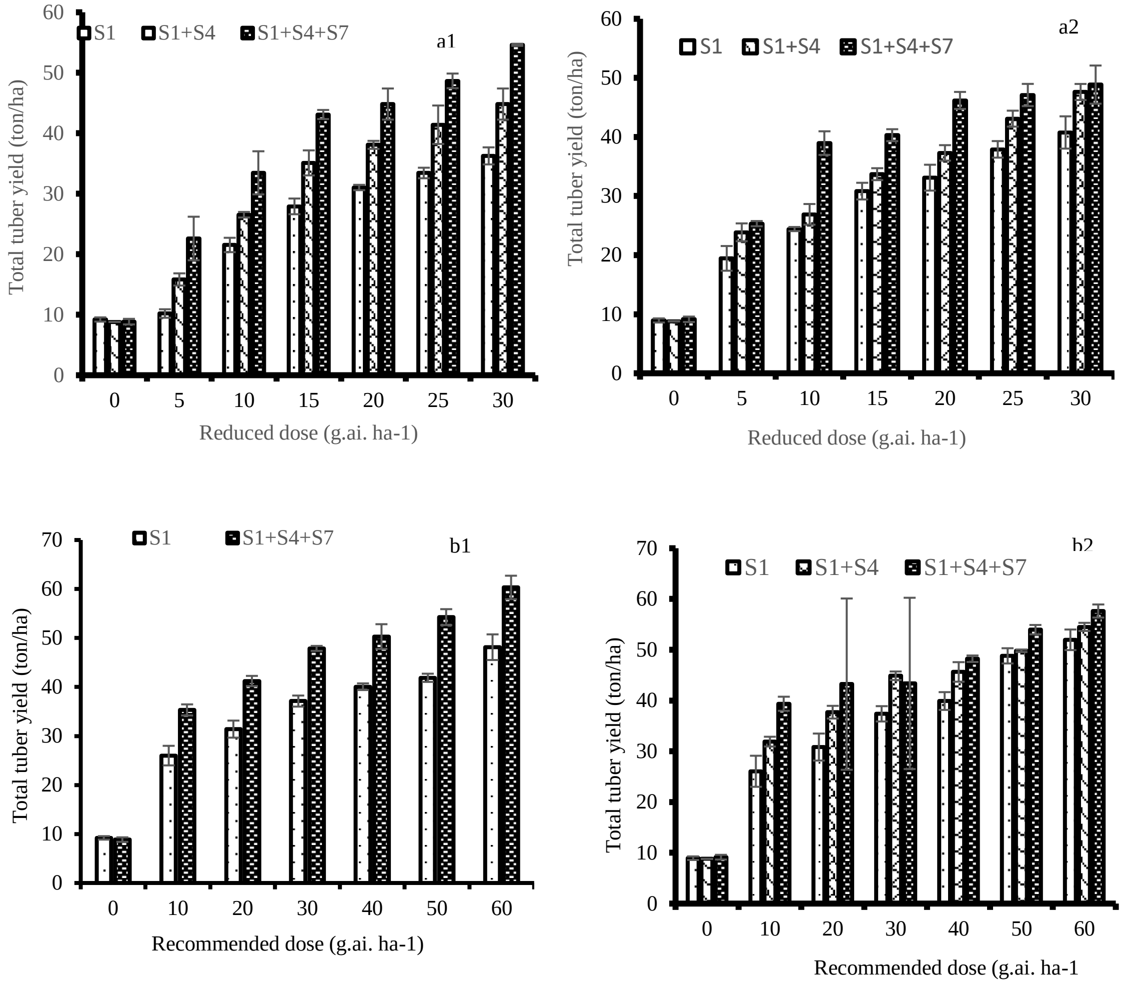

Figure 2. The effect of rimsulfuron application at a reduced dose (1X: 30 g a.i. ha^{-1}), (a); and a recommended dose (1X: 60 g a.i. ha-1), (b); without (1) and with (2) NIS surfactant (0.2 L ha-1) when applied at three cropping timings, on total tuber yield. The application timings (see Table 2) were as follows: i) S1: Leaf development; ii) S1+S4: leaf development (S1) + vegetatively propagated organs (S4); and iii) S1+S4+S7: leaf development (S1) + vegetatively propagated organs (S4) + Development of tuber (S7) (LSD=4.33).

4. Discussion

Historically, adjuvants are essential components for herbicide-resistant weeds control. To improve herbicides' performance or application objective, adjuvants are used in the spray tank [13]. These adjuvants are commonly added to the spray tank to improve herbicidal activity or application characteristics [39]. The results showed that rimsulfuron had adequate control of *C. album* and *A. retroflexus* in potato field. Tonks et al., [40] concluded post emergence application of rimsulforun at 18, 27 and 35 g ha^{-1} provided full control of *A. retroflexus* and 77, 84, and 91% of *C. album*, respectively. Also, Robinson et al., [11] reported post-application rimsulfuron at 9, 18, 27, 35, 70 g ha^{-1} controlled 67, 100, 100, 100, 100 % *A. retroflexus*, and 60, 90, 97, 90, 98% *C. album*. Similar results were reported by [41] concluded rimsulfuron at 18 g ha^{-1} post controlled *C. album* 77%. Also, increasing rimsulfuron doses up to 35 g a.i ha^{-1} enhanced *C. album* 91% and application 18, 27, 35 g ai. ha^{-1} of rimsulfuron post provided 100% control of *A. retroflexus*. Khatami et al., [42]

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reported that application of 30, 40 and 50 g ai. ha^{-1} provided 87.37, 99.75 and 96.87% reduction of *C. album* and 86.73, 89.91 and 95.50% of *A.retroflexus* biomass. Rimsulforun will be an effective post-emergence herbicide to make weed management system much better for potato production system.

The ranking of ED_{50} for the two species weeds was *C. album*> *A. retroflexus*. Herbicides efficiency was affected by weed species. The *C. album* produced much more biomass than *A. retroflexus* and was more tolerant to rimsulfuron. The results of our study are in line with the findings of [8,42,43]. The different responses of the two species suggest that there are 66% polar components in the leaf surface of *C. album*, in comparison with 55% for *A. retroflexus* [44]. In addition, the hair covering on the abaxial side of the *C. album* leaves and crystalline structure of hair led to less herbicide retention and penetration into the tissue of the plant while the *A. retroflexus* leaf surface has smooth cuticular [45]. Consequently, higher amounts of herbicide are required to be absorbed, transferred, and reach the target in the photosynthetic system in *C. album*. The angle of the spray droplet was 76º on the *C. album* leaves in comparison with 54° on *A. retroflexus* [44]. Weak herbicide performance of *C. album* was due to the leaf's surface lower wettability. The reduction of herbicide retention and absorption into the plant tissue leads to lower wettability [46].

For the enhanced activity of a post-emergent herbicide, high absorption and translocation are necessary. In addition, the active ingredient should be in optimum concentration and preserve its toxicity for the needed period. The lack of optimum concentration could lead to inadequate weed control [47]. Using the appropriate type of adjuvants is needed to increase the efficacy of most postemergence herbicides by, mostly, surface tension reduction [28]. For the individual reduced and recommened doses, the ED_{50} values for weeds biomass were much higher than combined surfactant. Therefore, they lead to a significantly greater herbicide efficacy and consequently a lower total herbicide dose to achieve a given effect. Our results were similar to previous studies e.g., [48,49]. Hutchinson *et al.*, [29] suggested that using NIS with rimsulforun controlled *C. album* and *A. retroflexus* by 89% and 97%, respectively. Tonks and Eberlin, [20] concluded that rimsulfuron applied at 4 different dosages (9, 18, 26, or 35 g/ ha) together with different types of surfactants such as a NIS, COC, a methylated seed oil (MSO), or an organosilicon surfactant (SIL), had a high (average 75%) control of common lambsquarters, regardless of adjuvant or dose. Mamnoii *et al.*, [50] concluded that the use of rimsulfuron (60 g ha^{-1}) + 2.5 % citowet (non-ionic surfactant) controlled *A. retroflexus* an average of 54% and 96% in Jiroft and Karaj of Iran in a two-year field experiments. The results showed that NIS was more effective to improve herbicidal performance and rainfastness on both weed species **(Table 3).** Increasing non-ionic surfactant concentration increased rimsulfuron activity around 11-fold for *Amaranthus retroflexus* compared to around 3-fold for *Chenopodium album.* Also reduced the rainfastness of rimsulfuron on *Amaranthus retroflexus* while improved the rainfastness of rimsulfuron on *Chenopodium album* **(Table 4).** Hammami et al., [35] reported that nonionic (Citogate) and cationic (Frigate) surfactant minimized the rainfall effect and improved the performance of clodinafop-propargyl on wild oat (*Avena fatua*). Based on these available results, it is possible to rank *Amaranthus retroflexus* the easiest wettable plant, followed by *Chenopodium album* [51]. Furthermore, the improvement of the tested rimsulfuron efficacy by non-ionic surfactant may be associated with a theory solubilizing, softening or disordering nature of cuticular waxes by non-ionic surfactant. It seems that the tested surfactant led to more cultivar penetration and stomal infiltration and subsequently, allowed better rimsulfuron absorption and translocation. Also, surfactants can make the surface tension lower for the spray droplet until concentration reaches to a point which is known as the Critical Micelle Concentration (CMC). The surface tension decreasing of the spray droplets caused by non ionic surfactant will not allow droplets bouncing off after reaching to the leaves in compare to ethylated seed oils [52,53]. Therefore, improving penetrability of active ingredient will increased he effect of herbicide and will reduced side effects risk [53].

5. Conclusions

Results demonstrated that utilization of a NIS surfactant enhanced rimsulfuron efficacy and rainfastness on *C. album* and *A. retroflexus.* Increasing non-ionic surfactant concentration from 0.04 to 1 L ha^{-1} increased rimsulfuron activity around 11-fold for *A. retroflexus* compared to around 3-fold for *C. album.* Also, increasing rimsulfuron dosages up to 60 g ai. ha^{-1} enhanced weed control to 100% at potato field and increased total tuber yield up to 60 ton ha-1. The application time was critical, however, post-application of rimsulfuron at S1+S4 and S1+S4+S7 stages of potato enhanced potato weed control and potato yield.

Author Contributions: Mohammad Taghi Alebrahim conceived the ideas. Mohammad Taghi Alebrahim and Elham Samadi Kalkhoran assembled the data, analyzed the data. Roghayyeh Majd and Asieh Khatami helped to interpret the data. Mohammad Taghi Alebrahim and Elham Samadi Kalkhoran wrote the manuscript. Mohammad Taghi Alebrahim edited the manuscript. Te-Ming Paul Tseng and Ilaias Travlos edited the manuscript. All authors improved and approved the manuscript.

Data Availability Statement: Data are available by contacting ESK (samadielham@uma.ac.ir).

Acknowledgments: This work was supported by the Faculty of Agriculture and Natural Resources, University of Mohaghegh Ardabili, Iran for financial support.

Conflicts of Interest: The authors declare that they have no conflict of interest.

Funding Information: The work was financed by the University of Mohaghegh Ardabili, Iran, and Mississippi State University, USA; also, this research received a grant from Mohammad Taghi Alebrahim and Te-Ming Paul Tseng.

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