

Effects of adjuvants on the effectiveness and rainfastness of rimsulfuron in potato (*Solanum tuberosum* L.)

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Abstract

The use of adjuvants is an effective way to improve weed control. We evaluated the effect of a non-ionic surfactant (NIS, Contact) and a crop oil concentrate (COC, Renol) on the efficacy and rainfastness of the rimsulfuron on redroot pigweed (*Amaranthus retroflexus* L.) and common lambsquarters (*Chenopodium album* L.) in pot studies as well as NIS surfactant in a potato under field conditions. In outdoor pot studies, NIS (0.15 L ha^{-1}) and COC (0.5 L ha^{-1}) did not improve the efficacy of rimsulfuron on *A. retroflexus* while they enhanced the performance and rainfastness of rimsulfuron 14 and two-fold on *Chenopodium album* at those rates, respectively. However, increasing the NIS concentration to 1 L ha^{-1} increased rimsulfuron efficacy by 11-fold for *A. retroflexus* compared to around 3-fold for *C. album*. The same treatment also reduced the rainfastness of rimsulfuron on *A. retroflexus* while improving the rainfastness of rimsulfuron on *Chenopodium album* compared to 0.04 L ha^{-1} . The ED_{50} and ED_{90} values indicated that the addition of the 0.2 L ha^{-1} of NIS improved the efficacy of both recommended (60 g ai. ha^{-1}) and the reduced (30 g ai. ha^{-1}) doses of rimsulfuron in field conditions. The highest potato yield (60 t ha^{-1}) was recorded when rimsulfuron was applied at recommended dose at three different crop growth stages including the development of leaves (S1), harvestable vegetative plants (S4), and tubers (S7), without using a NIS. Overall, the NIS improved rimsulfuron efficacy, especially when the herbicide was applied at a lower dose.

1. Introduction

Potato (*Solanum tuberosum* L.) is the fourth-largest crop in the world after wheat (*Triticum aestivum* L.), rice (*Oryza sativa* L.), and maize (*Zea mays* L.) (FAO, 2021). In Iran, potato is cultivated on 131,000 ha with total production over 4.6 million tonnes (Ministry of Agriculture-Jahad, 2022.). Weeds significantly decrease tuber yield, while weed control treatments (mainly herbicides) improve tuber yield (Chauhan, 2020). It is well documented that weed direct competition cause severe tuber yield reduction in potato crops (Modani et al. 2011; Mehring et al. 2016). For example, weed competition was reported to reduce the tuber yield by 33% and tuber quality by up to 86% (Bhullar et al. 2015). A diverse weed flora is associated with potato crops around the world making weed control extremely important to sustain good production levels. Globally, the most important weed species in potato include hairy nightshade (*Solanum sarachoides* L.), cut leaf nightshade (*Solanum triflorum* L.) (Eberlein et al. 1992), redroot pigweed (*Amaranthus retroflexus* L.) (Eleftherohorinos et al. 2000), common lambsquarters (*Chenopodium album* L.) (Lu et al. 2019), wild radish (*Raphanus raphanistrum* L.) (Ma et al. 2020) and rigid ryegrass (*Lolium rigidum* Gaud.) (Arsenault and Ivany, 2001). Unfortunately, most these species are resistant to some of the major herbicides used in potato crops. In Iran, a range of troublesome weeds including *C. album*, *A. retroflexus*, common knotgrass (*Polygonum avicular* L.), common purslane (*Portulaca oleracea* L.), common barnyard grass (*Echinochloa crus galli* (L.) P.Beauv.), green foxtail (*Setaria viridis* L.), *L. rigidum* and wall barley (*Hordeum leporinum* L.) impact potato production (Hasaninasab Farzane et al. 2018). However, *C. album* and *A. retroflexus* are the most problematic weed species in potato fields of Iran, causing the highest losses (Alebrahim et al. 2012; Azadbakht et al. 2017).

The farmers rely on a few different herbicide options to control these weeds in potato crops with varying degree of success. For instance, metribuzin, a common selective herbicide, has long been used to control a vast range of broadleaf and grass weeds in potato except for *Solanum sarrachoides* (Samadi Kalkhoran et al. 2021; Robinson et al. 1996). However, intensive use of this herbicide has led to the development of resistance to this chemical in several weed species (Alebrahim and Samadi Kalkhoran, 2017; Alebrahim et al. 2022). In addition, metribuzin can cause significant crop injury in certain potato cultivars, making it a risky option (Arsenault and Ivany, 2001). Rimsulfuron is another widely used post-emergence sulfonylurea herbicide with desirable properties such as high efficacy, broad-spectrum weed control, and low toxicity to mammalian organisms (Boyd and Dittmar, 2018). It inhibits acetolactate synthase (ALS), an important enzyme in the biosynthesis of branched-chain amino acids (leucine, isoleucine, and valine) in plants (Dayan et al. 2019). Rimsulfuron poses little to no acute toxicity hazard to mammals and has low toxicity to birds and honeybees (USEPA, 2007). More importantly, pre- and post-emergence applications of rimsulfuron have been reported to effectively control the most problematic weeds in potato such as *C. album* and *A. retroflexus* (Tonks and Eberlein, 2001; Alebrahim et al. 2021). However, weed control can be quite variable and patchy under sub-optimal environmental conditions. Therefore, it is important to optimize and improve the efficacy of important herbicides such as rimsulfuron to achieve maximum control and make them cost-effective options.

The appropriate application timing in relation to weed and crop growth (Samadi Kalkhoran and Alebrahim, 2016) and the use of appropriate, compatible adjuvants have been suggested as the most important factors in improving the herbicide efficacy (Hutchinson et al., 2004). An adjuvant is a biologically inert substance, but when added to herbicide spraying solutions, it may modify the surface characteristics of herbicide droplets, improve the bioavailability of the herbicide molecules, and change the diffusion coefficient of the herbicide molecules (Mehdizadeh and Alebrahim, 2015). It enhances retention, coverage, and efficacy of the applied herbicide (Green et al. 2007). Rimsulfuron needs an adjuvant to optimize its efficacy and rainfastness like other ALS herbicides (Mathiassen and Kudsk, 2002; Pannacci et al. 2010). Previous studies have indicated that the density, viscosity, surface tension, angle of contact, droplet size, and evaporation of the spray solution droplet could change with the addition of adjuvants to the spray solution (Cunha et al. 2009). Therefore, improving the retention capacity of droplets may be an approach aimed at increasing the herbicide efficacy and reducing its dose (Kudsk, 2008).

The type and the concentration of the applied adjuvant influence rimsulfuron activity. Different adjuvants including a nonionic surfactant (NIS), a crop oil concentrate (COC), a methylated seed oil (MSO) and an organosilicon surfactant (SIL) have proved useful in improving the efficacy of post-emergence applications of rimsulfuron (Eberlein et al. 1992). The MSO and NIS promote the foliar absorption and efficacy of rimsulfuron and several graminicides for grass weed control (Hutchinson et al. 2004).

Herbicide applications carry the risk of reduced efficacy if rainfall occurs shortly after application. Activators or surfactants modify herbicides characteristic such as viscosity, particle size and evaporation etc. which help improving the herbicide activity and rainfastness (Pacanowski, 2015; Kudsk et al. 1989).

Rainfastness is the time required for proper absorption to occur after the herbicide application so that, the herbicide activity is not diminished by precipitation (Molin and Hirase, 2005). Although previous studies have shown that adjuvants, particularly surfactants increase the herbicide efficacy (Rashed-Mihassel et al. 2009) and decrease the rainfastness of herbicides (Hammami et al. 2011), it is not clear whether different types of adjuvants are equally compatible with the concerned herbicides and equally effective. For example, there is no information on the comparative effects of NIS and COC on the efficacy and rainfastness of rimsulfuron in major weeds of potato.

To address this important research gap, we carried out two outdoor pot experiments and one field experiment. The objectives were to compare two different types of adjuvants (NIS and COC) for (i) their compatibility and effectiveness in improving rimsulfuron efficacy against two most problematic weed of potato crops i.e., *C. album* and *A. retroflexus*, and (ii) their ability to minimize the adverse effect of rainfall (reduction in herbicide efficacy) at different durations after rimsulfuron application. The objective of the field study was to evaluate the effectiveness of the NIS in increasing rimsulfuron efficacy against those two weeds at reduced doses of the herbicide applied at different crop growth stages in potato while also measuring the impact on tuber yield. The results of our study reveal the suitable adjuvant and its optimal dose to improve the efficacy of the herbicide rimsulfuron in potato crops.

2. Materials and Methods

A series of pot and field experiments was conducted to evaluate the effect of selected adjuvants under different conditions. Initially, two pot experiments were carried out outdoors at the Department of Agroecology, the University of Aarhus, Denmark (55° 19' N, 11° 23' E).

2.1. First outdoor pot experiment

Two major problematic, broadleaf weed species of potato crops were selected for two separate sub-experiments testing the efficacy of rimsulfuron at different rates with or without two surfactants under different timings of simulated rain. Seeds of *C. album* and *A. retroflexus* were obtained from the seed bank of the University of Aarhus, Denmark which had been collected from a local cropping field (55° 19' N, 11° 23' E). Twenty seeds of each *C. album* and *A. retroflexus* per pot were sown in 2 L plastic pots filled with a standard potting mixture which included sandy loam soil, sand, and peat (2:1:1 w/w/w, respectively) with 4.2% organic matter and a pH of 6.9. The pots were sub-irrigated five times a day with deionized water. Only four healthy plants were kept in each pot after seedling emergence and establishment. Weed plants were treated with the herbicide when they reached 4–6 leaf growth stage. The herbicide rimsulfuron (Titus DF, 250 g kg⁻¹, DuPont, Wilmington, DE, USA) was applied using a laboratory track sprayer equipped with two flat-fan nozzles (4110-14; Hardi; Taastrup, Denmark) working at 260 kPa pressure and delivering 155.3 L ha⁻¹. Plants were harvested three weeks after herbicide application and fresh and dry weights were recorded. For dry weight, all the plants harvested from a single pot were placed in paper bags and oven-dried at 75°C for 72 h before weighing.

The experiment was set up in a completely randomized design with a factorial arrangement and three replicates for each treatment combination. The treatments factors included rimsulfuron rates, surfactant type and the rain levels applied after herbicide application (Table 1). It is important to note that the experiments for both weed species were conducted independently and the herbicide rates chosen for both species differed based on local recommendations and preliminary range-finding tests (data not presented here). Two types of surfactants were chosen: a non-ionic surfactant (NIS), Contact (980 g/L linear alcohol ethoxylate, Nufarm, 0.15 L ha⁻¹, Wellington, New Zealand) and a crop oil concentrate (COC), Renol, 0.5 L ha⁻¹, Harrell's Chemical Company, FL, USA). Plants were subjected to 5 mm rain at different times (0, 1, 2, and 4 hours after treatment/HAT) by a rain simulator which was working at an intensity of 9 mm h⁻¹ (Pannacci et al. 2010). No simulated rain application was also included as a control treatment.

Table 1
List of treatments for all the experiments reported in the manuscript.

First outdoor pot experiment				
Species	Rimsulfuron (g ha ⁻¹)	Contact (NIS)	Renol (COC)	Rain
<i>Chenopodium album</i>	0, 1.875, 3.75, 7.5, 15, 30, 60	0, 0.15 L ha ⁻¹	0, 0.5 L ha ⁻¹	1, 2 ,4 HAT, no rain
<i>Amarathus retroflexus</i>	0, 0.2343, 0.468, 0.9375, 1.875, 3.75, 7.5	0, 0.15 L ha ⁻¹	0, 0.5 L ha ⁻¹	1, 2 ,4 HAT, no rain
Second outdoor pot experiment				
Species	Rimsulfuron (g ha ⁻¹)	Contact (NIS)	Renol (COC)	Rain
<i>Chenopodium album</i>	0, 1.875, 3.75, 7.5, 15, 30, 60	0, 0.04. 0.2, 1 L ha ⁻¹	-*	1, 2 ,4 HAT, no rain
<i>Amarathus retroflexus</i>	0, 0.2343, 0.468, 0.9375, 1.875, 3.75, 7.5	0, 0.04. 0.2, 1 L ha ⁻¹	-	1, 2 ,4 HAT, no rain
Field experiment (Reduced dose)				
Species	Rimsulfuron (g ai. ha ⁻¹)	Contact (NIS)	Renol (COC)	Application time
<i>Chenopodium album</i>	0, 5, 10, 15, 20, 25, 30	0.2 L ha ⁻¹	-	S1, S1 + S4, S1 + S4 + S7**
<i>Amarathus retroflexus</i>	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
<i>Chenopodium album</i>	0, 10, 20, 30, 40, 50, 60	0.2 L ha ⁻¹	-	S1, S1 + S4, S1 + S4 + S7
<i>Amarathus retroflexus</i>	0, 10, 20, 30, 40, 50, 60	0.2 L ha ⁻¹	-	S1, S1 + S4, S1 + S4 + S7
NIS: non-ionic surfactant, COC: crop oil concentrate, and HAT: hours after treatment.				
*Absent treatment; **For description of application timings at various potato growth stages in the field experiments (S1 to S7), see Table 2.				

Table 2

Major potato growth stages that are related to the application timings in the field experiments

Stage	Description
S0	Germination/sprouting/bud development
S1	Leaf development (main shoot)
S2	Formation of side shoots
S3	Stem elongation or rosette growth/shoot development (main shoot)
S4	Development of harvestable vegetative plant parts or vegetatively propagated organs (main shoot)
S5	Inflorescence emergence (main shoot) / heading
S6	Flowering (main shoot)
S7	Development of tuber
S8	Ripening or maturity of tuber and seed
S9	Senescence, beginning of dormancy
Based on Meier et al. (2009)	

2.2. Second outdoor pot experiment

A separate pot experiment was conducted with the same arrangements in which rimsulfuron doses, and the rain treatments were also kept the same. However, only NIS, Contact was used in this experiment at four different rates *viz.* 0, 0.04, 0.2, and 1 L ha⁻¹ for both *C. album* and *A. retroflexus*. Plants were harvested three weeks after herbicide application and fresh and dry weight were measured as described above.

2.3. Field experiments

Based on the results from pot experiments, two field experiments were conducted at Sheikh Kalkhoran of Ardabil (48° 20' N, 38° 15' E) in Iran, in a field containing loamy soil (42% sand, 32% silt, and 26% clay). Soil organic matter and pH were 0.9% and 7.68, respectively. Fertilizers were applied according to local soil test recommendations and were mixed with the irrigation water at various stages 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 in a well-tilled soil. Plots were sprayed with standard insecticides needed and were irrigated throughout the growing season with overhead sprinklers to maintain about 65% minimum soil water content.

Both field experiments were planned in a factorial arrangement using a randomized complete block design with three replicated blocks and a plot size of 2m × 4m. The first experiment had a series of reduced doses of rimsulfuron while the second one had a series of doses closer to the recommended

dose (Table 1). Only NIS, Contact was used at two different rates in both experiments and was applied at different crop growth stages. These experiments also focused on *C. album* and *A. retroflexus* just like pot experiments. Rimsulfuron (Titus DF, 250 g kg⁻¹, DuPont, Wilmington, DE, USA) was applied by using a back-pack sprayer equipped with two flat-fan nozzles (8001; Inter) worked at 260 kPa and delivered 250 L ha⁻¹.

Weed control was evaluated by harvesting weed plants within a quadrat of 0.75 m × 0.50 m at three weeks after treatment. Three weeks after herbicide application, all of the weed plants in each plot were harvested and dried in an oven at 75°C for 72 h and then weighed. Total tuber yield consisted of the weight of tubers harvested manually from the center rows of plot area and the weight of previously taken samples, both converted to t ha⁻¹.

2.4. Statistical Analyses

The dose-response data from all experiments were analyzed using the R program (Version 4.0.1) (R Core Team, 2020) with the drc package (Version 4.0.1). Dose response curves were fitted on dry weight data of *C. album* and *A. retroflexus* using a three parameters log-logistic regression model (Streibig et al. 1993):

$$y = \frac{d}{1 + \exp(b(\log(z) - \log(ED_{50}))}$$

1

where y is dry weight of z , d is the upper limit where the dose is zero, ED_{50} denotes the dose required for reducing dry weight by half, and b is proportional to the slopes of the curves around ED_{50} . The ED_{50} parameter in Eq. (1) can be replaced by any ED level (Pannacci and Covarelli, 2009), (e.g., ED_{10} , ED_{90}).

The relative potency (RP) is the horizontal displacement between two curves at a chosen ED_x (Kudsk et al. 1989). The biological exchange rate in a single application, i.e., the relative potency between the herbicides was calculated as follows:

$$RP = ED_{50xf} / EDC_{50xf+v} \quad (2)$$

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 was 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 analysis of variance (ANOVA) was performed using PROC GLM (PC-SAS) and when the F Test indicated significant effects, means were compared using least significant difference (LSD) Fisher ($P < 0.05$) test.

3. Results

3.1. First outdoor pot experiment

In this experiment, no significant improvement in rimsulfuron efficacy against *A. retroflexus* was observed due to addition of both NIS (0.15 L ha^{-1}) and COC (0.5 L ha^{-1}) surfactants (comparing ED_{50} values of the 'no rain' treatments) (Table 3). In contrast, the inclusion of the NIS adjuvant significantly improved the performance of rimsulfuron on *C. album* (Table 3). Both NIS and COC improved rainfastness of rimsulfuron in *C. album* (Table 3). In *C. album*, the ED_{50} doses were much higher in comparison with *A. retroflexus* and the NIS strongly improved the efficacy of rimsulfuron. It also had a strong effect on rainfastness while no significant impact of rain with COC was observed except in case of 4 HAT (Table 3).

Table 3

The effect of NIS and COC surfactants on the efficacy and rainfastness of rimsulfuron applied on *Amaranthus retroflexus* and *Chenopodium album* at various timings. Relative rainfastness is the necessary length of a rain-free period following herbicide application. The ED₅₀ values for each species sharing different letters differed significantly according to LSD test ($P < 0.05$)

<i>Amaranthus retroflexus</i>				
Surfactant	Rain	ED ₅₀ (g ha ⁻¹)	ED ₅₀ 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
0.15 L ha ⁻¹ NIS	No rain	0.26 ^{ab}	0.182–0.345	1.00
	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
<i>Chenopodium album</i>				
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
NIS (0.15 L ha ⁻¹)	No rain	1.89 ^a	1.11–2.69	1.00

<i>Amaranthus retroflexus</i>				
	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
COC (0.5 L ha ⁻¹)	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

The rainfastness was low without any adjuvant and also in the presence of COC, however, it improved significantly when NIS was added and reached its maximum value after 4 HAT in *A. retroflexus* (Table 3). Relative rainfastness was the highest after 4 hours.

3.2. Second outdoor pot experiment

In the second experiment, it was observed 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, surfactant increased rimsulfuron efficacy 11-fold compared to rimsulfuron 0.04 L ha⁻¹ on *A. retroflexus*. 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 3-fold compared to rimsulfuron 0.04 L ha⁻¹ on *C. album* which was less compared to *A. retroflexus* (Table 4).

Table 4

The effect of NIS adjuvant doses on the efficacy and rainfastness of rimsulfuron applied at various timings on *Amaranthus retroflexus* and *Chenopodium album*. Relative rainfastness is the necessary length of a rain-free period following herbicide application. The ED₅₀ values for each species sharing different letters differed significantly according to LSD test ($P < 0.05$).

<i>Amaranthus retroflexus</i>				
Surfactant	Rain	ED ₅₀ (g ha ⁻¹)	ED ₅₀ 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
<i>Chenopodium album</i>				
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

<i>Amaranthus retroflexus</i>				
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

Increasing concentration of the NIS also improved the rainfastness of rimsulfuron on *C. album*. Regarding herbicidal performance, the NIS was less efficient on *C. album* compared to *A. retroflexus*, but when tested for rainfastness it showed more activity, especially at 1 L ha⁻¹ for *C. album* (Table 4). The NIS efficacy was much higher compared to Renol.

3.3. Field experiments

The results showed that when rimsulfuron was combined with 0.2 L ha⁻¹ NIS, *C. album* and *A. retroflexus* control was only slightly increased. For ED₅₀ values, the curves' upper limits were different for various doses and application times for each species, in some cases, the curves were crossing (Tables 5, 6). The ED₅₀ values of rimsulfuron were significantly reduced in two and three times of *A. retroflexus* at reduced dose of rimsulfuron. The ranking of ED₅₀ at reduced doses for the three application times was S1 > S1 + S4 > S1 + S4 + S7 with and without surfactant (Table 5). Based on the ED₅₀ values, surfactants improved rimsulfuron efficacy especially at reduced doses compared to the sole application of rimsulfuron (Table 5). The ED₅₀ values at reduced doses and various time of application for *C. album* were higher than *A. retroflexus* (Table 5). Table 6 presents the ED₅₀ ranking of the efficacy of the three application times at the recommended dose of the *C. album* and *A. retroflexus* dose-response curves.

Table 5

The estimated regression parameters for *Amaranthus retroflexus* and *Chenopodium album* dry weight in response to reduced rimsulfuron dose (30 g a.i. ha⁻¹), applied with and without NIS surfactant (1L ha⁻¹).

The application timings correspond to different potato growth stages as explained in Table 2. The response variable was 0-100% weed control (dry weight reduction). The ED₅₀ values for each species sharing different letters differed significantly according to LSD test ($P < 0.05$). The Relative potency (RP) has been explained in section 2.4.

<i>Amaranthus retroflexus</i> dry weight at reduced dose without surfactant						
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
<i>Amaranthus retroflexus</i> dry weight at reduced dose with surfactant						
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
<i>Chenopodium album</i> dry weight at reduced dose without surfactant						
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
<i>Chenopodium album</i> dry weight at reduced dose with surfactant						
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

Table 6

The estimated regression parameters for *Amaranthus retroflexus* and *Chenopodium album* dry weight in response to the recommended dose of rimsulfuron (60 g a.i. ha⁻¹), applied with and without NIS surfactant (1L ha⁻¹). The application timings correspond to different potato growth stages as explained in Table 2. The response variable was 0-100% weed control (dry weight reduction). The ED₅₀ values for each species sharing different letters differed significantly according to LSD test ($P < 0.05$). The Relative potency (RP) has been explained in section 2.4.

Application time	<i>Amaranthus retroflexus</i> dry weight at the recommended dose without surfactant					
	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 + S4	-6.18 ± 8.04	100.02 ± 0.37	4.67 ± 4.61	6.67 ± 3.49 ^a	9.51 ± 0.61	2.07
S1 + S4 + S7	-6.73 ± 49.78	100.00 ± 0.36	3.87 ± 27.11	5.37 ± 24.61 ^a	7.44 ± 16.14	1.14
<i>Amaranthus retroflexus</i> dry weight at the recommended dose with surfactant						
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 + S4	-2.37 ± 1.25	100.21 ± 0.68	1.27 ± 1.36	3.21 ± 1.86 ^a	8.11 ± 0.87	1.00
S1 + S4 + S7	-6.00 ± 43.54	100.00 ± 0.39	3.24 ± 26.42	4.67 ± 25.69 ^a	6.74 ± 19.15	1.00
<i>Chenopodium album</i> dry weight at the recommended dose without surfactant						
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 + S4	-2.85 ± 0.23	102.37 ± 1.43	5.30 ± 0.34	11.44 ± 0.30 ^a	24.68 ± 1.83	0.88
S1 + S4 + S7	-3.10 ± 0.87	100.43 ± 1.27	3.54 ± 1.02	7.18 ± 0.67 ^a	14.57 ± 1.71	0.83
<i>Chenopodium album</i> dry weight at the recommended dose with surfactant						
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 + S4	-0.24 ± 0.25	170.19 ± 145.92	0.001 ± 0.005	12.86 ± 89.96 ^a	9.79 ± 1.56	1.00
S1 + S4 + S7	-7.19 ± 26.69	100.00 ± 2.00	6.32 ± 10.72	8.58 ± 4.82 ^a	1.16 ± 6.68	1.00

The results of rimsulfuron on *C. album* dry weight showed that surfactant could not improve the efficacy of recommended dose of rimsulfuron at S1 + S4 and S1 + S4 + S7 (Table 6). The estimated ED₅₀ 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 was added to this herbicide. The 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 times and recommended doses at S1 stage.

The highest potato yield (60 t ha⁻¹) was obtained when 60 g ai. ha⁻¹ rimsulfuron was applied at three stages (S1, S4, and S7) without using the NIS (Fig. 3). However, no significant differences were recorded in terms of potato yield when the same dose of rimsulfuron was applied at the three (S1, S4, and S7) and two (S1, S4) stages with NIS (Fig. 1).

4. Discussion

Rimsulfuron is a widely used post-emergence sulfonylurea herbicide in potato crops (Alebrahim et al. 2021). Extensive usage of the ALS inhibitors causes environmental side effects. Therefore, optimizing the application techniques must be used to overcome this problem. A solution to the negative impacts of continuous application of ALS herbicides is to use adjuvants (Mehdizadeh and Alebrahim, 2015). Historically, adjuvants have been used as spray tank mixtures to enhance the herbicide application activity or application characteristics and hence, the efficacy (Khatami et al. 2017). The results of this study demonstrate that adjuvants vary in their effectiveness in improving the efficacy and rainfastness of rimsulfuron. Our results showed that NIS significantly improved performance and rainfastness of rimsulfuron in *C. album*.

Previous studies have shown that the NIS improved the efficacy of rimsulfuron (Hutchinson et al. 2004). Increasing the concentration of the NIS up to 1 L ha⁻¹ improved the performance of rimsulfuron 11 and 3-fold compared to rimsulfuron 0.04 L ha⁻¹ on *A. retroflexus* and *C. album*, respectively. Rimsulfuron applied at 4 different doses (9, 18, 26, or 35 g ha⁻¹) showed improved activity against *C. album* when different surfactants such as a NIS, COC, a methylated seed oil (MSO), and an organosilicon surfactant (SIL) were added to the herbicide (Tonks and Eberlin, 2001). In the current study, ED₅₀ values of rimsulfuron were greater for *C. album* than those for *A. retroflexus*. This kind of variable response is common across different weed species. It might be because *C. album* is less susceptibility of *A. retroflexus* plants. These findings are consistent with some previous studies (Khatami et al. 2017; Arianezhad et al. 2017). It has been suggested that there are 66% polar components in the surface of *C. album* leaves, compared to 55% for *A. retroflexus* (Harr et al. 1991). Furthermore, polar component and capillary coverage of the abaxial side of the *C. album* leaves and the crystalline structure of the hair may have reduced the retention and penetration of herbicide into the tissue of the plant while the *A. retroflexus* leaf surface has a smooth cuticular (De Ruiter et al. 1990). As a result, it was necessary to absorb, transfer, and translocate higher rates of herbicide into the photosynthetic system of *C. album* leaves. It

has also been reported that the spray droplet was at an angle of 76° on the leaves of the *C. album* as opposed to 54° angle on *A. retroflexus* leaves (Harr et al. 1991). Lower surface tension can improve herbicide spray wettability by reducing the contact angle between water droplets and leaves (Costa et al. 2017). The poor herbicide efficacy on *C. album* was also potentially caused by the lower wettability of the leaf surface. Reduced retention and uptake of herbicides into the plant tissue reduces wettability (Ramsdale and Messersmith, 2001).

It is evident that *A. retroflexus* was easily wettable plant compared to *C. album* (Ren et al. 2007). Improvement of the tested rimsulfuron efficacy by non-ionic surfactant may be associated with better chemical solubilizing, softening, or disordering nature of cuticular waxes by the surfactant. It is possible that this surfactant led to more cuticular penetration and stomal infiltration of the herbicide molecules which allowed overall superior absorption and translocation of rimsulfuron. It has been reported that the non-ionic surfactants can make the surface tension lower for the spray droplets until concentration reaches a point known as the critical micelle concentration (CMC). At this point, the decreased surface tension does not allow spray droplets to bounce off after reaching the leaves in comparison to ethylated seed oils (Sharma et al. 1996; Penner, et al. 2007). Therefore, improved penetrability of the active ingredient increases the efficacy of the herbicide and minimizes the off-target damage risk (Penner, et al. 2007).

The spray deposition on the surface of the leaf is strongly related to the cuticular structure and the chemical identity tendency adjuvant to retention on the leaf. Therefore, an appropriate surfactant is often required for optimal absorption of sulfonyl urea herbicides like rimsulfuron (Stagnari et al. 2007). For optimal 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 (Hess and Richard, 1990). Using the appropriate type of adjuvants is needed to increase the efficacy of most post-emergence herbicides by, mostly, surface tension reduction (Kudsk, 2008). In this study, for the without reduced and recommended doses, the ED₅₀ values for weeds biomass were much higher than with surfactant. Therefore, they lead to a significantly higher herbicide efficacy and therefore to a lower total herbicide dose to obtain the given effect.

The use of reduced doses of herbicides is a contentious issue, but sometimes quite practical to reduce unnecessary crop injury and environmental effects. Some of the major reasons to support lower doses include: (i) registered doses are set to ensure adequate control over a wide spectrum of weed species, weed densities, growth stages, and environmental conditions, so may not be required in each case, (ii) maximum weed control is not always necessary for optimal crop yields (Zhang et al. 2000). Several studies have demonstrated good weed control with reduced herbicide doses (Boström and Fogelfors, 2002; Hamil et al. 2004). Therefore, the doses lower than recommended dose have been evaluated to reduce side effect of rimsulfuron in potato field. For example, post-emergence applications of rimsulfuron at 18, 27 and 35 g ha⁻¹ were reported to provide 100% control of *A. retroflexus* and 77, 84 and 91% of control of *C. album*, respectively (Tonks and Eberlein, 2001). In another study, rimsulfuron application at

different rates ranging from 18 to 70 g ha⁻¹ all provided 100% control of *A. retroflexus* and 90 to 98% of *C. album* (Robinson et al. 1996). Renner and Powell (1998) also reported similar results where a post-emergence application of rimsulfuron at 18 g ha⁻¹ provided 77% control of *C. album* in potato crop while doubling this dose achieved up to 91% control of that weed. On the other hand, *A. retroflexus* was more susceptible to rimsulfuron with a 100% control achieved with 18 to 35 g ai. ha⁻¹. In a separate study, application of rimsulfuron at 30 to 50 g ai. ha⁻¹ provided 87 to 99% reduction in *C. album* and 87 to 95% reduction in *A. retroflexus* biomass (Khatami et al. 2017). In Iran, rimsulfuron (60 g ha⁻¹) + 2.5% citowet, another NIS, provided up to 96% control of *A. retroflexus* (Mamnoii et al. 2016).

5. Conclusions

The non-ionic surfactant enhanced rimsulfuron efficacy and rainfastness on both *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% in potato crop under field conditions while achieving the highest tuber yield of up to 60 t ha⁻¹. The application time was critical, however, post-application of rimsulfuron at S1 + S4 and S1 + S4 + S7 stages of potato achieved the highest level of weed control and produced the highest potato yield.

Declarations

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Figures

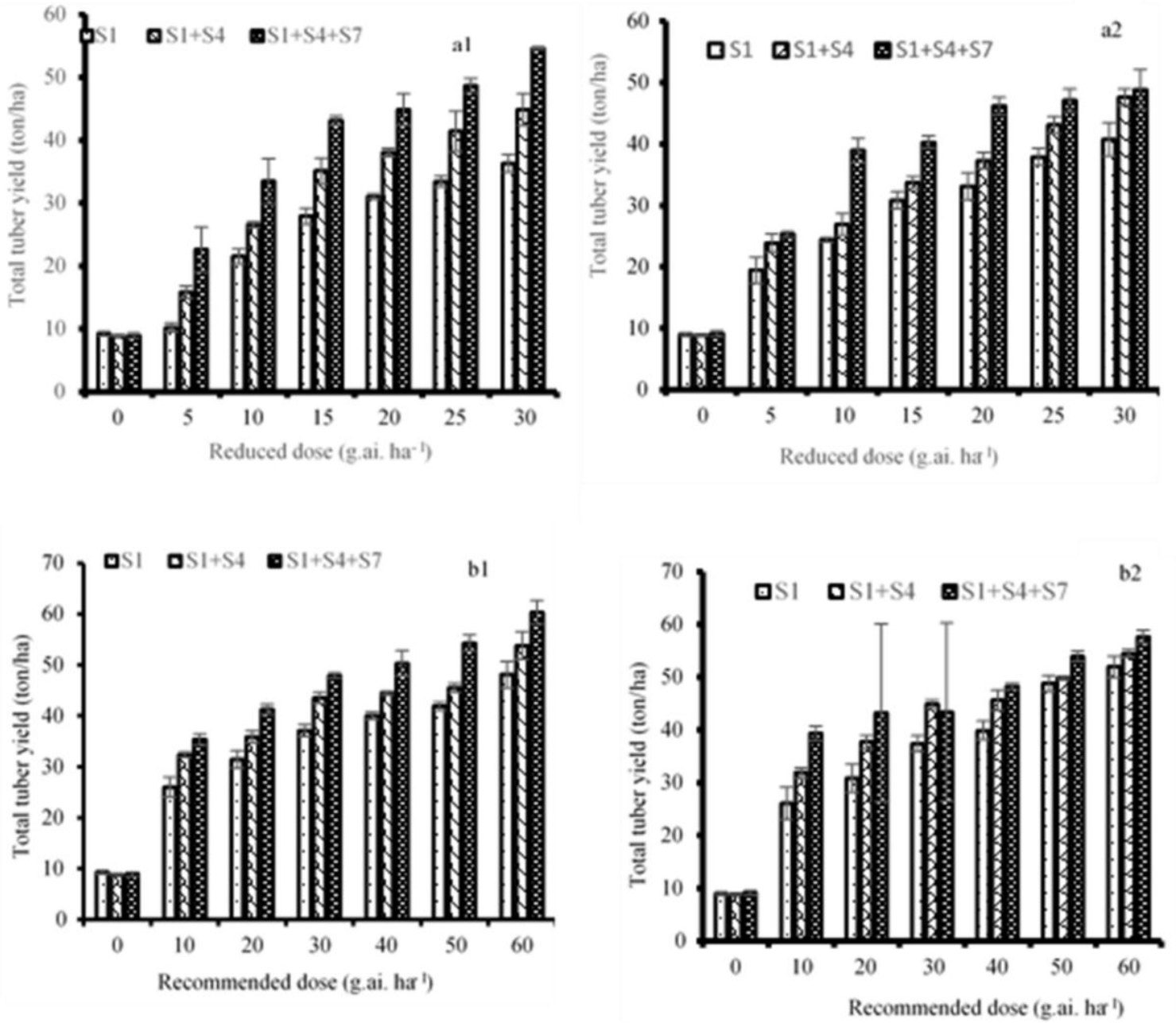


Figure 1

The effect of rimsulfuron application at a reduced dose (30 g a.i. ha⁻¹), (a); and a recommended dose (60 g ai. ha⁻¹), (b); without (1) and with (2) NIS surfactant (0.2 L ha⁻¹) when applied at three different 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)