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Research Article

Effect of water hardness induced by bicarbonate and chloride forms of magnesium and sodium on the performance of herbicides for littleseed canarygrass control

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Abstract: Based on the chemical properties of herbicide and carrier water, water hardness might have different impacts on herbicide performance. A study was conducted in the greenhouse to determine the effect of chloride and bicarbonate forms of Mg^{+2} and Na^{+} on the performance of clodinafop-propargyl and sulfosulfuron for littleseed canarygrass control. The concentrations of bicarbonate and chloride forms of Mg^{+2} and Na^{+} had no significant effect on the ED_{50} of clodinafop-propargyl. The relative potency of clodinafop-propargyl, in the presence of all mineral salts, was 1.0 or had no significant difference from 1.0. On the contrary, increasing the mineral salts reduced the ED_{50} of sulfosulfuron significantly, especially in the presence of bicarbonate forms of Mg^{+2} and Na^{+}. In this regard, the relative potency of sulfosulfuron as affected by 100 to 800 ppm $Mg(HCO_3)_2$ was about 0.5 to 0.7 times higher than control. This value was increased from 0.5 to 2.2 at 100 to 800 ppm sodium bicarbonate. Hence, the ranking of the mineral salts on improving sulfosulfuron performance was $NaHCO_3 > Mg(HCO_3)_2 > MgCl_2 > NaCl$. It is suggested that because of the lipophilic nature of clodinafop-propargyl, the presence of mineral salts did not affect the performance of this herbicide. It is concluded that, in determining the effect of water hardness on herbicide performance, in addition to chemical properties of herbicide, type of mineral salt, and its concentration, it is also essential to know the changes in the pH of the carrier water due to the mineral salts.

Keywords: ED_{50}, herbicide efficacy, lipophilic herbicide, *Phalaris minor*, water quality

Introduction

Many factors affect the performance of herbicides, such as formulation, physicochemical properties of the molecule (especially log K_{ow} (Octanol/Water Partition Coefficient and pK_a or [-log10 (K_a) (acid dissociation constant)], morphology and physiology of weeds, application time, and environmental conditions at the time of application and quality of their carriers (Mirzaei *et al.*, 2022). As a universal solvent, water is considered the most critical and common carrier in most herbicides, and the performance of herbicide molecules is influenced by water quality (Devkota and Johnson, 2016). Indices of carrier water quality, such as hardness, turbidity, pH, and temperature, can vary with the geographical location and water sources (Devkota *et al.*, 2016; Schortgen and Patton, 2020). Therefore, the water

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hardness is effective in optimizing herbicide efficacy. Existing cations in water (as a common carrier) can alter herbicide efficacy (Devkota and Johnson, 2016), meaning that it can affect the absorption, translocation, and optimum performance of some herbicides for weed control (Green and Cahill, 2003; Holm and Henry, 2005; Bernards *et al.*, 2005; Green and Hale, 2005).

Characteristics such as high level of hardness attributed to Ca^{2+} and Mg^{2+}, high pH, suspended solids, organic matter and clay (turbidity), and bicarbonates in water in some parts of Iran have significantly reduced the efficacy of some herbicides and thus increased their application rate (Jabbari and Zand, 2007).

The effects of different salts in hard water on the phytotoxicity of herbicides vary depending on the type of cation, herbicide, and weed species (Nalewaja *et al.*, 1989; Mirzaei *et al.*, 2019). These effects include synergistic, antagonistic, and neutral (Nalewaja *et al.*, 1989). In this regard, it has been suggested that applicators avoid using Mn-containing fertilizers when applying 2,4-D dimethylamine, because the adjuvant does not favorably overcome antagonism (Patton *et al.*, 2016). Furthermore, antagonistic effects of Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} on the amine form of 2,4-D herbicide have been reported (Nalewaja *et al.*, 1991). The presence of cations such as Ca^{+2}, Mg^{+2}, and Fe^{+3} in the water used in the sprayer tank reduces the herbicide's solubility by binding the cations to the negative part of herbicide molecules and, as a result, causing their deposition in the sprayer tank. The plant does not readily absorb the resulting salts, so the herbicide will not provide sufficient biological activity to control weeds (Thelen *et al.*, 1995; Penner, 2006). In general, it is believed that hard water reduces the efficacy of some essential herbicides such as glyphosate and 2,4- D (amine form) with weak acid nature (high pK_a) (Petroff, 2000; Holm and Henry, 2005). Mg^{2+}, Fe^{+3}, Ca^{2+}, and Na^{+} ions bind with glyphosate molecules in hard water, preventing them from binding to the EPSPS (5-enolpyruvylshikimate-3-phosphate synthase) enzyme. Consequently, the herbicide efficacy is reduced (Mirzaei *et al.*, 2022). Some studies have also shown the sensitivity of bentazone, dicamba, MCPA, 2,4-D, and sethoxydim to water hardness (Petroff, 2000). Should the carrier water have a high mineral content and with high pH. In that case, the amount of cations binding to the negatively charged herbicide molecules will increase due to the higher dissociation (ionization) of the herbicide. As a result, herbicide efficacy will decrease (Jordan *et al.*, 2011).

The addition of Mg^{2+} as fertilizer to the spraying tank containing glyphosate affected the efficacy of this herbicide and had antagonistic effects on glyphosate absorption and translocation in velvetleaf *Abutilon theophrasti* Medik. (Bernards *et al.*, 2005). Scroggs *et al.* (2009) also showed that weed control efficiency significantly decreased where glyphosate was applied at the recommended dose with the Zn^{+} containing fertilizer (Scroggs *et al.*, 2009). Nalewaja and Matysiak (2000) showed that using 800 ppm Ca^{2+} in the spray solution had an antagonistic effect on nicosulfuron phytotoxicity. Devkota and Johnson (2019) reported that water at an alkaline pH and the presence of hard water cations could negatively affect the performance of dicamba and glyphosate for control of common lambsquarters *Chenopodium album* L., Palmer amaranth *Amaranthus palmeri* S.Watson, and pitted morningglory *Ipomoea lacunosa* L.

Littleseed canarygrass *Phalaris minor* Retz. is an annual grass weed belonging to Poaceae family that is considered as one of the most dominant weeds in many parts of the world and the second most-frequent grass weed in wheat *Triticum aestivum* L. fields of Iran (Gherekhloo *et al.*, 2020). This weed can reduce a high percentage of wheat grain yield (Duary and Yaduraju, 2005; Chhokar *et al.*, 2006). Afentouli and Eleftherohorinos (1999) reported that densities of 152 and 304 (per m^2) littleseed canarygrass decreased the wheat yield by 32 and 42%. The repeated application of ACCase inhibiting herbicides has led to the evolution of resistant biotypes, which has significantly impacted the spread of littleseed canarygrass populations (Raghav *et al.*, 2016). More than one million hectares of wheat fields in Iran have been infested with herbicide-resistant weed biotypes, including *Avena sterilis* subsp. *ludoviciana*, *Phalaris minor*, and *Lolium rigidum* have becomeresistant to

ACCase-inhibiting herbicides (Gherekhloo *et al.*, 2016).

Accordingly, this study evaluated the effects of chloride and bicarbonate forms of Mg^{2+} and Na^{+} cations and their concentrations on the efficacy of clodinafop-propargyl and sulfosulfuron as the commonly applied herbicides in wheat fields of Iran for littleseed canarygrass control.

Materials and Methods

Plant material

A greenhouse experiment was performed to evaluate the effects of chloride and bicarbonate forms of Mg^{2+} and Na^{+} cations on the efficacy of clodinafop-propargyl (Topik® EC 8%) and sulfosulfuron (Apyrus® WG 75%) herbicides on littleseed canarygrass. Littleseed canarygrass seeds (approximately 300 seeds per spike) were collected from the Ferdowsi University of Mashhad research farm in April 2016, located in the southeast of Mashhad (36º15´ N, 59º 28´ E, altitude 985 m).

Sowing of plants

Seeds were sterilized with 5% sodium hypochlorite for four minutes and then rinsed with distilled water for three minutes. For breaking dormancy, seeds were immersed in sulfuric acid (98%) for three minutes and then kept in Petri dishes containing filter paper with 5 ml distilled water for 72 h in a refrigerator at 4 °C in the dark condition (Golmohammadzadeh *et al.*, 2019). Fifty seeds were placed in a 9 cm petri dish covered with filter paper (Whatman#1). Petri dishes with germinated seeds were put into a growth chamber calibrated for a 26/18 °C day/night, 12-h photoperiod at 800 μmol m^{-2} s^{-1} of light intensity and 60% relative humidity until transplanting. Ten germinated seeds were planted at 1 cm depth in pots (14 cm diameter × 11 cm height) containing substrate with 40 % clay, 40% sand, and 20% perlite to maintain soil moisture. The pots were irrigated daily as needed. Seedlings were thinned to four plants pot^{-1} at the two-leaf stage. The pots were placed in a research greenhouse with a 25 °C day/15 °C night temperature regime under the natural photoperiod.

The experiment was repeated at a one-week interval starting in August 2016 at Ferdowsi University of Mashhad-Iran.

Experiment 1: Determination of effective dose

The 90% effective dose (ED_{90}) of clodinafop-propargyl and sulfosulfuron for littleseed canarygrass control was determined under greenhouse conditions based on dose-response experiments. The experiment was conducted as a factorial based on a randomized complete block design with four replications. Experimental factors included two herbicides, clodinafop-propargyl, and sulfosulfuron, at seven rates of 0, 3.125, 6.25, 12.5, 25, 50, 100% of the recommended field dose (clodinafop propargyl 0.8 L ha^{-1} and sulfosulfuron 26.6 g ha^{-1}) (Zand *et al.*, 2008). A dose of herbicide that resulted in 90% reduction in fresh weight of littleseed canarygrass (ED_{90}) was determined and used for the second experiment as a recommended dose in greenhouse conditions.

Experiment 2: Dose-response experiments

These experiments were conducted as a randomized complete block design in factorial arrangement with three replications for clodinafop-propargyl and sulfosulfuron herbicides. Experimental factors were herbicide dose at seven levels (0, 6.25, 12.5, 25, 50, 100, and 200% of the recommended dose obtained from the first experiment), and four salt types ($NaHCO_3$, $Mg(HCO_3)_2$, NaCl, and $MgCl_2$), at five levels (0, 100, 200, 400 and 800 ppm). The treatments were prepared so that 500 mg of each mineral salt was first dissolved in one liter of deionized water and completely dissolved by a mixer. Thirty minutes after dissolving mineral salts, the pH of the solution was measured by a portable pH meter (MPH-200 model, MARMONIX ®, Canada) with four replicates for each solution. Then, each herbicide was added to the solutions prepared at the abovementioned doses.

Immediately after mixing, herbicide treatments were applied at the 4-6-leaf stage weeds using an automatically fixed sprayer (air pump sprayer) equipped with a TeeJet

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8002 flat fan nozzle with a spraying width of 1 m (spray output rate of 195 L ha^{-1} at a pressure of 250 kPa).

Four weeks after the herbicide spraying, the above-ground live plants were cut at the soil surface, and the fresh weight was measured.

Statistical analysis

There was no significant difference between the two-time runs of each experiment; therefore, data were pooled over experimental runs and averaged for analysis.

Data were analyzed using regression analysis. This analysis was done by fitting the data to a four-parameter (Equation 1) and three-parameter log-logistic function (Equation 2) (Streibig 1988; Ritz and Streibig 2005).

$$Y = c + \frac{d - c}{1 + \exp\{b(\log(x) - \log(e))\}} \qquad \text{(Eq. 1)}$$

Where Y is the response (fresh weight) at dose x, c is the lower limit of the curve, d is the upper limit of the curve, e is the ED_{50}, and b is the relative slope around the point e. This function is symmetric around point e.

$$Y = \frac{d}{1 + \exp\{b(\log(x) - \log(e))\}} \qquad \text{(Eq. 2)}$$

This equation is used when the response rate at the highest applied dose is close to zero, and its parameters are similar to the previous function. The ED_{50} parameter was determined after ensuring the suitability of the function (Streibig, 1988). Then the relative potency value for different concentrations of $NaHCO_3$, $Mg(HCO_3)_2$, NaCl, and $MgCl_2$ were determined using Equation 3.

$$\text{Relative potency} = \frac{\text{Deionized water ED50}}{\text{Hard water ED50}} \qquad \text{(Eq. 3)}$$

Data analysis of two experiments was performed using R software (ver. 3.5.3) and drc package (Ritz and Streibig, 2005).

Results

Determination of effective dose

Results of the first experiment, four weeks after treatment with clodinafop-propargyl and sulfosulfuron, revealed that increasing the concentration of both herbicides decreased the fresh weight of littleseed canarygrass (Fig. 1, a and b). However, the slope of the fresh weight loss curve of sulfosulfuron was steeper than clodinafop-propargyl. In other words, the results of ED_{50} obtained from the parameters estimated by the three-parameter log-logistic model indicated that the littleseed canarygrass was more susceptible to sulfosulfuron than clodinafop-propargyl (Table 1).

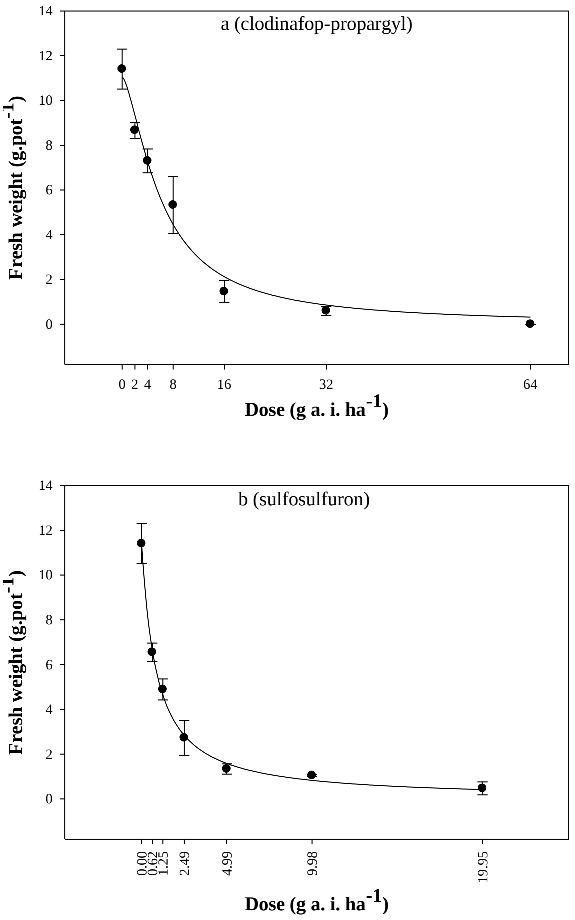

Figure 1 Response of fresh weight of littleseed canarygrass to different doses of clodinafop-propargyl (a) and sulfosulfuron (b) four weeks after herbicide treatment under greenhouse conditions. Data points are observed by means of six replicates. Estimated parameters are given in Table 1. The error bars indicate standard error (SE).

The required doses of clodinafop-propargyl to reduce 50 and 90% of littleseed canarygrass fresh weights compared to the untreated control were 6.15 and 26.53 g.ha^{-1}, and for sulfosulfuron were 0.86 and 7.12 g.ha^{-1}, respectively (Table 1). Accordingly, the dose required to reduce 90% (ED_{90}) of littleseed canarygrass fresh weight was recommended in greenhouse conditions for the herbicides.

Table 1 Parameters of the three-parameter log-logistic model of clodinafop-propargyl and sulfosulfuron herbicides based on fresh weight of littleseed canarygrass four weeks after treatment in greenhouse conditions.

Herbicide	Slope (b) (±SE)	The upper limit (d) (±SE) (g pot^{-1})	ED_{50} (±SE) (g a.i. ha^{-1})	ED_{90} (±SE) (g a.i. ha^{-1})
Clodinafop-propargyl	1.50 (0.15)	11.05 (0.42)	6.15 (0.59) **	26.53 (3.54) **
Sulfosulfuron	1.04 (0.06)	11.39 (0.23)	0.86 (0.05) **	7.12 (0.81) **

SE: Standard Error, **: significant at $p \leq 0.01$. d is the upper limits of the curves; the ED_{50} is the effective doses which caused 50% fresh weight reduction of littleseed canarygrass, and b is the slope of the curve around ED_{50}, respectively.

pH of mineral salts solution

Increasing the mineral salts had a different effect on the pH of the carrier water (Fig. 2). Adding 100 ppm of $Mg(HCO_3)_2$ increased the pH of the carrier water from 8 to 10. While increasing 100 ppm of $MgCl_2$ and NaCl reduced the carrier water's pH from 8 to about 6.5. Increasing the $NaHCO_3$ concentration did not significantly affect the pH of the carrier water. Also, the pH changes trend did not differ significantly with increasing salt concentrations compared to 100 ppm.

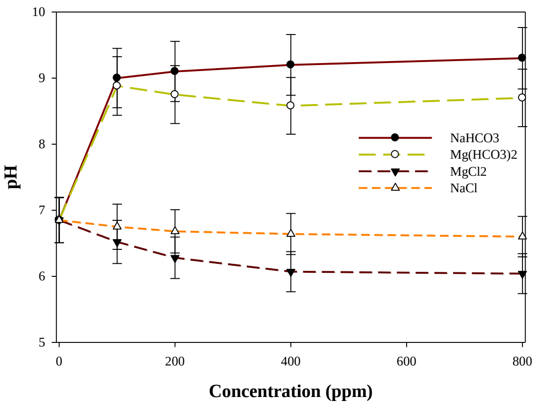

Figure 2 Relationship between mineral salt concentrations and pH of carrier water. Data points are observed by means of four replicates. The error bars indicate standard error (SE).

Dose-response experiments

The experiment's results revealed that increasing the concentration of Magnesium chloride did not change the clodinafop-propargyl efficacy. In other words, the ED_{50} of clodinafop-propargyl was almost constant at different concentrations of $MgCl_2$ (Table 2).

Changes in ED_{50} in clodinafop–propargyl treatment were distinct under the influence of $Mg(HCO_3)_2$ concentrations. The highest ED_{50} was observed at 100 ppm and the lowest at 800 ppm (9.34 and 3.94 g a.i. ha^{-1}) (Table 2).

At 100 and 200 ppm NaCl, the ED_{50} of clodinafop-propargyl was increased, indicating a decrease in herbicide efficacy. However, the overall increase in NaCl and $NaHCO_3$ concentrations were similar. Chloride and bicarbonate forms of Mg^{2+} cation had little effect on the ED_{50} of clodinafop-propargyl (Table 2).

The relative potency of clodinafop-propargyl showed that different concentrations of $MgCl_2$ did not significantly change this index (Fig. 3, a). In other words, the relative potency index at most concentrations of Mg^{2+} was 1.00. Changes in the relative potency values of clodinafop-propargyl were different in the presence of different concentrations of Mg(HCO3)2 (Fig. 3, b). The relative potency of 100 ppm Mg(HCO3)2 was 0.5, indicating a 50% reduction in herbicide efficacy at 100 ppm Magnesium bicarbonate. Based on the standard error, the efficacy of clodinafop -propargyl was not affected by adding different concentrations of Magnesium chloride.

Considering the standard error values at other concentrations, herbicide efficacy did not change significantly, and herbicide efficacy was not affected by magnesium bicarbonate. At 100 and 200 ppm NaCl, the efficacy of clodinafop-propargyl was approximately reduced by 30% (Fig. 3, c).

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Table 2 Parameters of the three-parameter log-logistic model of clodinafop-propargyl herbicide based on fresh weight of littleseed canarygrass in the presence of mineral salts, four weeks after treatment under greenhouse conditions.

Mineral salt	Concentration (ppm)	Slope (b) (±SE)	The upper limit (d) (±SE) (g pot^{-1})	ED$_{50}$ (±SE) (g a.i. ha^{-1})	95% Confidence intervals for ED$_{50}$	
$MgCl_2$	0 (deionized water)	0.63 (0.06)**	11.28 (0.44)**	4.91 (0.88)**	4.03	5.79
	100	0.56 (0.06)**	11.37 (0.43)**	4.24 (0.82)**	3.42	5.06
	200	0.75 (0.07)**	11.42 (0.43)**	5.06 (0.74)**	4.32	5.8
	400	0.76 (0.07)**	11.36 (0.43)**	4.88 (0.72)**	4.16	5.6
	800	0.62 (0.06)**	11.53 (0.42)**	4.72 (0.73)**	3.99	5.45
$Mg(HCO_3)_2$	0 (deionized water)	0.68 (0.06)**	11.16 (0.51)**	5.18 (0.97)**	4.21	6.15
	100	0.87 (0.08)**	11.45 (0.48)**	6.34 (1.31)**	5.03	7.65
	200	0.84 (0.07)**	11.34 (0.49)**	4.87 (0.72)**	4.15	5.59
	400	0.88 (0.07)**	11.75 (0.47)**	6.42 (0.82)**	5.6	7.24
	800	0.56 (0.05)**	11.40 (0.50)**	3.94 (0.82)**	3.12	4.76
NaCl	0 (deionized water)	0.56 (0.04)**	11.37 (0.22)**	4.77 (0.57)**	4.2	5.34
	100	0.84 (0.06)**	11.35 (0.22)**	6.55 (0.56)**	5.99	7.11
	200	0.97 (0.06)**	11.55 (0.21)**	6.99 (0.52)**	6.47	7.51
	400	0.65 (0.05)**	11.41 (0.22)**	4.21 (0.44)**	3.77	4.65
	800	0.77 (0.06)**	11.38 (0.22)**	4.13 (0.38)**	3.75	4.51
$NaHCO_3$	0 (deionized water)	0.67 (0.06)**	11.19 (0.51)**	5.12 (0.97)**	4.15	6.09
	100	0.68 (0.06)**	11.51 (0.49)**	4.51 (0.76)**	3.75	5.27
	200	0.72 (0.06)**	11.55 (0.48)**	5.53 (0.89)**	4.64	6.42
	400	0.88 (0.07)**	11.41 (0.49)**	5.42 (0.76)**	4.66	6.18
	800	0.65 (0.06)**	11.34 (0.50)**	5.28 (0.70)**	4.58	5.98

SE: Standard Error, **: significant at $p \leq 0.01$. ED$_{50}$ was separated using its 95% confidence intervals (CI) and those followed by the same letter are not significantly different at $p \leq 0.05$. 4. d is the upper limits of the curves; the ED$_{50}$ is the effective doses which caused 50% fresh weight reduction of littleseed canarygrass, and b is the slope of the curve around ED$_{50}$, respectively.

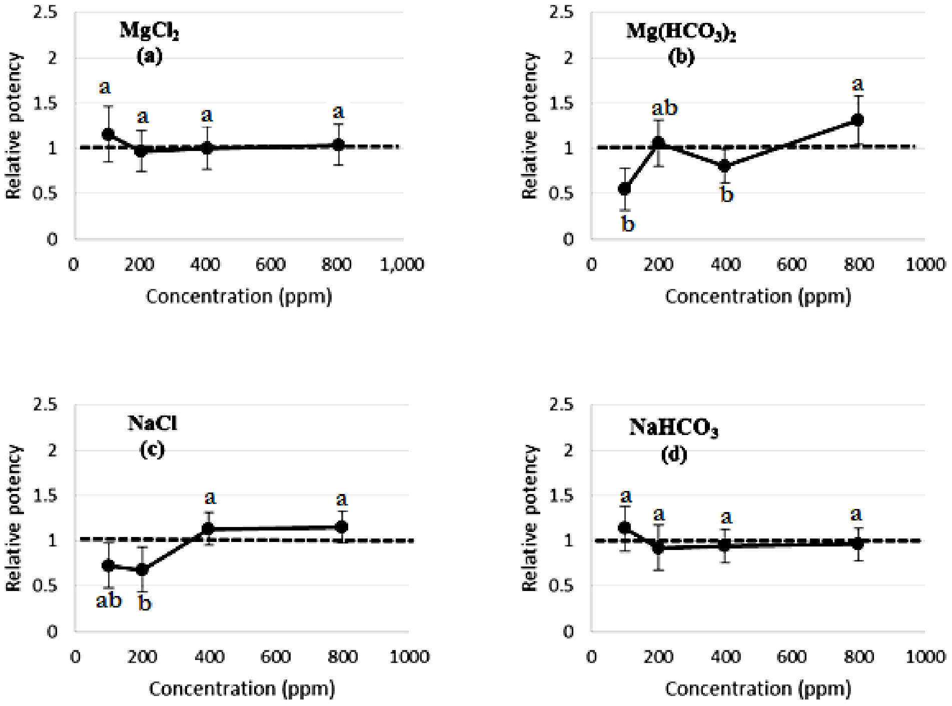

Figure 3 Relative potency of clodinafop-propargyl herbicide at different concentrations of (a) Magnesium chloride, (b) Magnesium bicarbonate, (c) Sodium chloride, and (d) Sodium bicarbonate. The bars indicate standard error (SE). The dashed line represents the relative potency =1.00.

At higher concentrations of NaCl, the presence or absence of the mentioned salt had no significant effect on the relative potency index, which confirms the different herbicidal responses of clodinafop-propargyl to NaCl concentration. Although at different $NaHCO_3$ concentrations, no significant differences were observed in the relative potency of clodinafop-propargyl, this value was less than 1.00 for 200, 400, and 800 ppm $NaHCO_3$ (Fig. 3, d).

Increasing $MgCl_2$ concentration decreased ED_{50} of sulfosulfuron (Table 3). The highest and lowest ED_{50} belonged to concentrations of 100 ppm (0.36 g a.i. ha^{-1}) and 800 ppm (0.20 g a.i. ha^{-1}). Therefore, the presence of this salt in the water of the sprayer tank increased the herbicide performance of sulfosulfuron. The increase of $Mg(HCO_3)_2$ concentration significantly decreased ED_{50} of sulfosulfuron (Table 3). The highest and lowest ED_{50} was observed at 0 ppm (0.33 g a.i. ha^{-1}) and 800 ppm (0.19 g a.i. ha^{-1}) magnesium bicarbonate. Sulfosulfuron efficacy was also affected by increasing the concentration of chloride and bicarbonate forms of Na^+ cation in the spraying tank so that with increasing the concentration of salts, ED_{50} of sulfosulfuron decreased. The highest and lowest ED_{50} herbicides were observed at 200 ppm (0.39 g a.i. ha^{-1}) and 800 ppm (0.23 g a.i. ha^{-1}) NaCl and 0 ppm (0.33 g a.i. ha^{-1}) and 800 ppm (0.15 g a.i. ha^{-1}) Sodium carbonate, respectively (Table 3). At 800 ppm sodium bicarbonate, ED_{50} decreased by more than 50% compared to the control, indicating the increase in the efficacy of sulfosulfuron under alkaline conditions in the sprayer tank.

The relative potency of sulfosulfuron increased significantly with an increase in $MgCl_2$ concentration (Fig. 4, a). The relative potency of sulfosulfuron increased 0.15, 0.45, and 0.75 fold by increasing $MgCl_2$ concentration to 200, 400, and 800 ppm compared to herbicide application without Magnesium chloride, respectively. Also, $Mg(HCO_3)_2$ increased the relative potency of sulfosulfuron (Fig. 4, b). Relative potency at 100, 200, 400, and 800 ppm $Mg(HCO_3)_2$ were about 0.5, 0.6, 0.7, and 0.7 times more than control, respectively, indicating the increment of herbicide efficacy on fresh weight of littleseed canarygrass. Also, the addition of NaCl to the sprayer tank increased the relative potency of sulfosulfuron about 0.4 times at 800 ppm compared to the control treatment (Fig. 4, c). Besides, the relative potency increased with $NaHCO_3$ (Fig. 4, d). The relative potency at 100, 200, 400, and 800 ppm was about 0.5, 0.6, 0.6, and 2.2 times compared to the control treatment, respectively.

Table 3 Parameters of the three-parameter log-logistic model of sulfosulfuron herbicide based on fresh weight of littleseed canarygrass in the presence of different concentrations of mineral salts, four weeks after treatment in greenhouse conditions.

Mineral salt	Concentration (ppm)	Slope (b) (± SE)	The upper limit (d) (± SE) (g pot^{-1})	ED_{50} (± SE) (g a.i. ha^{-1})	95% Confidence intervals for ED_{50}	
$MgCl_2$	0 (deionized water)	0.60 (0.05) **	11.47 (0.46) **	0.35 (0.07) **	0.28	0.42
	100	0.55 (0.04) **	11.44 (0.46) **	0.36 (0.07) **	0.29	0.43
	200	0.52 (0.04) **	11.43 (0.46) **	0.30 (0.07) **	0.23	0.37
	400	0.51 (0.05) **	11.38 (0.46) **	0.24 (0.06) **	0.18	0.30
	800	0.49 (0.04) **	11.39 (0.46) **	0.20 (0.05) **	0.15	0.25
$Mg(HCO_3)_2$	0 (deionized water)	0.59 (0.03) **	11.48 (0.38) **	0.33 (0.05) **	0.28	0.38
	100	0.41 (0.03) **	11.40 (0.38) **	0.22 (0.03) **	0.19	0.25
	200	0.41 (0.03) **	11.40 (0.38) **	0.21 (0.03) **	0.18	0.24
	400	0.41 (0.03) **	11.39 (0.38) **	0.20 (0.03) **	0.17	0.23
	800	0.40 (0.03) **	11.39 (0.38) **	0.19 (0.02) **	0.17	0.21
NaCl	0 (deionized water)	0.58 (0.04) **	11.50 (0.59) **	0.32 (0.07) **	0.25	0.39
	100	0.45 (0.04) **	11.47 (0.59) **	0.35 (0.10) **	0.25	0.45
	200	0.55 (0.04) **	11.43 (0.59) **	0.39 (0.09) **	0.30	0.48
	400	0.40 (0.04) **	11.43 (0.59) **	0.30 (0.07) **	0.23	0.37
	800	0.37 (0.04) **	11.41 (0.59) **	0.23 (0.02) **	0.21	0.25
$NaHCO_3$	0 (deionized water)	0.71 (0.05) **	11.42 (0.18) **	0.33 (0.04) **	0.29	0.37
	100	0.39 (0.03) **	11.39 (0.18) **	0.22 (0.03) **	0.19	0.25
	200	0.36 (0.03) **	11.40 (0.18) **	0.22 (0.03) **	0.19	0.25
	400	0.32 (0.03) **	11.40 (0.18) **	0.20 (0.03) **	0.17	0.23
	800	0.32 (0.04) **	11.40 (0.18) **	0.15 (0.02) **	0.13	0.17

SE: Standard Error, **: significant at $p \leq 0.01$. ED_{50} was separated using its 95% confidence intervals (CI) and those followed by the same letter are not significantly different at $p \leq 0.05$. 4. d is the upper limits of the curves; the ED_{50} is the effective doses which caused 50% fresh weight reduction of littleseed canarygrass, and b is the slope of the curve around ED_{50}, respectively.

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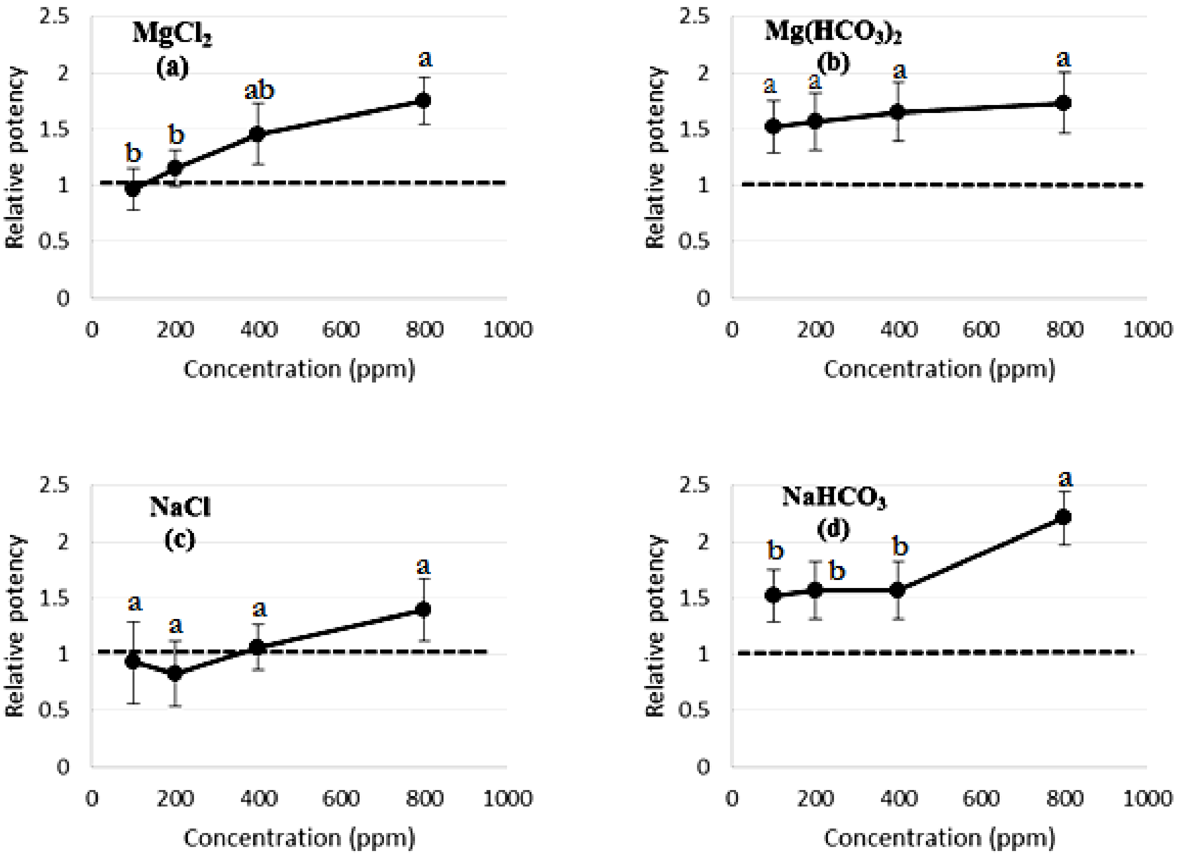

Figure 4 Relative potency of sulfosulfuron herbicide at different concentrations of (a) Magnesium chloride, (b) Magnesium bicarbonate, (c) Sodium chloride, and (d) Sodium bicarbonate. The dashed line represents the relative potency = 1.00. The error bars indicate standard error (SE).

Discussion

A comparison of the results revealed that clodinafop-propargyl performance based on the reduction in fresh weight of the littleseed canarygrass was not sensitive to concentrations of all mineral salts in the sprayer tank. Likewise, similar experimental results showed that calcium chloride in hard water did not affect the efficacy of 2,4-D in controlling horseweed *Conyza* sp. (Roskamp *et al.*, 2013). Although many experiments have reported that water hardness reduces herbicide efficacy (Holm and Henry, 2005; Devkota *et al.*, 2016; Mirzaei *et al.*, 2019), various factors such as the lipophilicity of herbicides can play a role in herbicide efficacy. Ramsey *et al.* (2005) indicated that lipophilic herbicides are less sensitive to changes in spraying conditions such as water hardness. Therefore, because of having log K_{ow}= 3.9 and lipophilic properties (Lewis *et al.*, 2016), clodinafop-propargyl is probably less affected by water hardness.

In the present experiment, the efficacy of sulfosulfuron improved with increasing concentration of mineral salts, especially bicarbonate forms of Mg^{2+} and Na^{+} cations, and at high concentrations. For example, at 800 ppm $NaHCO_3$ concentration, the efficacy of sulfosulfuron on the fresh weight of littleseed canarygrass was 2.2 times more than the control treatment. On the other hand, the relative potency of sulfosulfuron at 800 ppm of this salt reached its maximum. As the $NaHCO_3$ and $Mg\ (HCO_3)_2$ concentration increased, the pH of carrier water increased

(Fig. 2), which resulted in a decrease in the ED_{50} or an increase in the performance of the sulfosulfuron. The solubility of herbicides in the sulfonylurea group increases under alkaline conditions (Matocha and Senseman, 2007). These herbicides are commonly sold as weak acids, and their solubility in water directly relates to the pK_a of a hydrogen atom on the urea bridge (Green and Cahill, 2003). The pKa of sulfosulfuron is 3.51; then, its water solubility is low when the pH of the spray solution is below the pK_a, and the product forms a dispersion.

On the other hand, when the herbicide is at a low concentration and solubility is not a limiting factor, the low pH of the spray solution increases herbicide absorption; however, when the concentration increases and solubility is limiting, then higher pH increases herbicide absorption (Green and Hale, 2005). Sarmah and Sabadie (2002) showed that increasing the concentration of salts in the sprayer tank increases pH, ionization, and absorption in the cuticle wax and ultimately improves the efficacy of herbicides in the sulfonylureas group. Green and Cahill (2003) reported that biological activity of nicosulfuron was much greater on common cocklebur *Xanthium strumarium* when mixed with pH adjusters (e.g. sodium carbonate) that increase pH. However, the depletion effect of cations on herbicide efficacy has been reported (Devkota *et al.*, 2016). Also, based on the fact that with increasing pH, sulfosulfuron herbicide with log K_{ow}= -0.77 has a more favorable transfer to the phloem due to its pka, which increases its efficacy in the alkaline state (Cobb and Reade, 2011; Singh and Singh, 2012). As the $MgCl_2$ and NaCl concentration increased, the carrier water pH decreased, slightly increasing the relative potency of sulfosulfuron in the presence of $MgCl_2$. In contrast, the relative potency of sulfosulfuron was not affected by NaCl concentration. It was suggested that the increase in the relative potency of sulfosulfuron in the presence of $MgCl_2$ was probably due to the high H^+ concentration and decreased ionization and dissociation of this weak acid herbicide, which increases penetration through the cuticle, as well as herbicide performance.

Green and Hale (2005) stated that increasing and decreasing pH can increase nicosulfuron biological activity, depending on weed species and spray conditions. In this regard, the study of the efficacy of nicosulfuron on crabgrass *Digitaria sanguinalis* L. showed that adding factors that increase the pH of the herbicide solution increased its solubility and, ultimately, its efficacy and control (Green and Cahill, 2003). Also, Woznica *et al.* (2001) showed that sulfosulfuron efficacy to green foxtail was greatly enhanced when applied in an alkaline spray mixture (pH 7.4–8.2) compared to pH 4.0–5.7 unbuffered spray solution. In this regard, it has been reported that increasing the pH of trifloxysulfuron increased the uptake and translocation of the herbicide. The increase of approximately two units of pH compared to pk_a resulted in uptake and displacement of herbicide trifloxysulfuron, which improved the uptake, transport, and efficacy of this herbicide in *Amaranthus palmeri* S.Watson. and *Caperonia palustris* (L.) A.St.-Hil (Matocha *et al.*, 2006). Therefore, the pH of spraying water is one of the most important factors affecting the efficacy of herbicides, especially sulfonylurea herbicides (Devkota and Johnson, 2019). In general, the relative potency of sulfosulfuron in the presence of all mineral salts indicated that the herbicide efficacy was higher in the presence of different concentrations of $NaHCO_3$ than other salts ($NaHCO_3$ > $Mg(HCO_3)_2$> $MgCl_2$ > NaCl).

Conclusions

Our results indicated that the herbicide type plays an essential role in determining the performance of herbicides under water hardness conditions. For example, a lipophilic herbicide like clodinafop-propargyl was less affected by water hardness. In other words, the change of the carrier water pH by mineral salts did not affect clodinafop-propargyl performance. Contrary to

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this, the performance of sulfosulfuron increased significantly under high pH arising from a high concentration of bicarbonate forms of magnesium and sodium and at low pH resulting from high concentrations of $MgCl_2$. However, high mineral salts eventually block or clog the spray nozzles, reducing spraying uniformity. As such, herbicide spray performance is indirectly affected by water hardness, and weed control is not optimized. Hence, if there is a requirement to increase herbicides' efficiency and compensate for cations' adverse effects, adjuvants are considered a more logical solution.

Disclosure Statement

The authors declare that there are no interests to declare.

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اثر سختی آب ناشی از فرم‌های بی‌کربنات و کلرور کاتیون‌های منیزیم و سدیم بر کارایی علف‌کش‌ها برای کنترل علف قناری

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چکیده: براساس خواص شیمیایی علف‌کش و آب حامل، سختی آب ممکن است اثرات متفاوتی بر کارایی علف‌کش داشته باشد. برای ارزیابی تأثیر فرم‌های کلرید و بی‌کربنات منیزیم و سدیم روی کارایی کلودینافوپ‌پروپارژیل و سولفوسولفورون در کنترل علف قناری، یک مطالعه گلخانه‌ای انجام شد. غلظت فرم‌های بی‌کربنات و کلرید کاتیون‌های منیزیم و سدیم تأثیر معنی‌داری بر ED_{50} کلودینافوپ‌پروپارژیل نداشت. پتانسیل نسبی کلودینافوپ پروپارژیل در حضور تمام نمک‌های معدنی یک بود یا با یک تفاوت معنی‌داری نداشت. برعکس، افزایش غلظت نمک‌های معدنی باعث کاهش قابل‌توجهی در ED_{50} سولفوسولفورون، به‌ویژه در حضور فرم بی‌کربنات منیزیم و سدیم شد. در این راستا، پتانسیل نسبی سولفوسولفورون تحت تأثیر غلظت‌های ۱۰۰ تا ۸۰۰ پی‌پی‌ام $Mg(HCO_3)_2$ حدود ۰/۵ تا ۰/۷ برابر بیشتر از شاهد بود. این مقدار در غلظت‌های ۱۰۰ تا ۸۰۰ پی‌پی‌ام بی‌کربنات سدیم به ۰/۵ تا ۲/۲ افزایش یافت. ازاین‌رو، رتبه‌بندی نمک‌های معدنی در افزایش کارایی سولفوسولفورون $NaHCO_3 > Mg(HCO_3)_2 > MgCl_2 > NaCl$ بود. به‌دلیل ماهیت لیپوفیلی کلودینافوپ پروپارژیل، وجود نمک‌های معدنی بر عملکرد این علف‌کش تأثیرگذار نبود. بنابراین، در تعیین اثر سختی آب بر کارایی علف‌کش، علاوه‌بر ویژگی‌های شیمیایی علف‌کش، نوع نمک معدنی و غلظت آن، درک تغییرات pH آب حامل به‌دلیل نمک‌های معدنی مهم است.

واژگان کلیدي: علف‌کش چربی‌دوست، کارایی علف‌کش، کیفیت آب، ED_{50}، *Phalaris minor*

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