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ORIGINAL ARTICLE

Performance of 2,4-D plus MCPA and Mesosulfuron plus Iodosulfuron plus Mefenpyr-diethyl as influenced by ammonium sulfate, urea ammonium nitrate, and carrier water hardness

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Abstract Carrier water quality is an essential consideration for enhancing herbicide performance. Water hardness can negatively affect some herbicides. Two separate dose-response experiments were conducted to investigate the effect of carrier water hardness and ammonium sulfate (AMS) and urea ammonium nitrate (UAN) as adjuvants on the performance of 2,4-D plus MCPA and mesosulfuron plus iodosulfuron plus mefenpyr-diethyl. The experimental factors included herbicide rates at five levels (63.3, 126.6, 253.1, 506.3 and 1012.5 g a. i. ha^{-1} for 2,4-D plus MCPA and 1.125, 2.25, 4.5, 9 and 18 g a. i. ha^{-1} for mesosulfuron plus iodosulfuron plus mefenpyr-diethyl), carrier water hardness based on concentrations of $CaCO_3$ at five levels (0, 250, 500, 750, and 1000 mg L^{-1}), and tank-mix of ammonium sulfate (AMS) and urea ammonium nitrate (UAN) as adjuvants at three levels (0, 1%, and 2% [w/v]). The results indicated that increased carrier water hardness up to 500 mg L^{-1} did not affect the performance of 2,4-D plus MCPA for wild mustard control. However, water hardness higher than 500 mg L^{-1} led to a reduction in the herbicide performance. The application of AMS and UAN was effective on the performance of 2,4-D plus MCPA herbicide in controlling wild mustard and overcame the negative effects of carrier water hardness. The performance of mesosulfuron plus iodosulfuron plus mefenpyr-diethyl herbicide in controlling wild mustard was not affected by carrier water hardness. In the case of herbicides such as mesosulfuron plus iodosulfuron plus mefenpyr-diethyl, which are not sensitive to carrier water hardness, the use of 2% AMS or UAN may also increase herbicide performance.

Keywords Adjuvant · Antagonism · Hard water · Herbicide performance

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Introduction

Wild mustard (*Sinapsis arvensis* L.) is a broadleaf and annual winter weed of the Brassicaceae family. It has indeterminate upright growth and may reach a height of more than two and a half meters (Siyahpoosh et al., 2012). Due to the stability of seed banks, high ability for competition and growth, and its high reproductivity, wild mustard is permanent and persistent in most regions of the world. The high potential of developing reproduction, seed production, and seed germination characteristics results in a wide dispersal of this weed (Singh et al., 2022). Wild mustard is one of the most critical weeds in wheat fields, distributed

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as a broadleaf and winter annual weed in most parts of Iran, and damages autumn crops (Shahbazi et al., 2019).

Herbicides are now considered major and essential inputs of agricultural systems in developed countries. Hence, crop yield depends significantly on the application of herbicides (Han et al., 2020). Reduced herbicide performance for any reason will result in increased costs through additional cultivation needs or repeated sprays. Conversely, poor weed control following herbicide applications increases doubts about potential herbicide resistance and also reduces users' confidence in herbicide applications (Naylor, 2002).

Because water is the most important and common liquid carrier for herbicide applications, its quality plays an important role in their performance. Since the mid-1980s, research has indicated that the performance of weak-acid herbicides is affected by cations existing in hard water (Mcmullan, 2000). Hard water is described as water containing high levels of calcium, magnesium, sodium, or iron cations (Altland, 2001; Petroff, 2000). These ions all have a positive charge and the potential to bond with the negatively charged molecules of the herbicide, thus preventing their efficiency, absorption, and translocation (Devkota et al., 2016).

In some references, the criteria for water hardness are the amount of calcium and magnesium ions which is stated based on the gram equivalent of calcium carbonate (Holm & Henry, 2005; Brown, 2006). The presence of cations such as Ca^{2+}, Mg^{2+}, Fe^{2+} and Fe^{3+} in the spray water reduces the solubility of herbicide salts by bonding to the negative structure of herbicide molecules, which leads to their deposition in the sprayer tank (Devkota et al., 2016). The resultant salt is not easily absorbed by the plant and will not possess enough bioactivity for weed control (Penner, 2006; Thelen et al., 1995). Antagonistic minerals can inactivate the postemergence herbicides, including glyphosate, synthetic auxins such as 2,4-D (not esters), ACCase inhibitors, ALS inhibitors, 4-HPPD inhibitors, and glutaminesynthetase inhibitors (Zollinger et al., 2010).

In recent years, much research has been conducted on the effects of different concentrations of minerals available in water and herbicide efficacy. Nosrati et al. (2012) reported that calcium chloride and magnesium chloride reduce the efficacy of 2,4-D plus MCPA herbicide in controlling *Glycyrrhiza glabra* L. In another experiment, Mirzaei et al. (2017) investigated the role of water hardness in the efficacy of 2,4-D herbicide in controlling *Amaranthus retroflexus* L. and *Bassia scoparia* (L.) AJ Scott. Their results indicated that hard water reduces the efficacy of 2,4-D herbicide in controlling these two weed species.

Not all herbicides are affected by water hardness. The effect of water quality on herbicide efficacy depends on the physical and chemical properties. Calcium ions have been reported to reduce the efficacy of many herbicides such as sethoxydim (Matysiak & Nalewaja, 1999; Mirzaei et al., 2016), glufosinate ammonium (Maschhoff et al., 2000; Devkota & Johnson, 2016), clethodim (Nandula et al., 2007), imazamethabenz (Hsiao et al., 1996), imazethapyr (Gronwald et al., 1993), 2,4-D (Nalewaja et al., 1991; Roskamp et al., 2013; Mirzaei et al., 2017), and glyphosate (Nalewaja & Matysiak, 1991; Altland, 2001; Baily et al., 2002; Christian, 2003; Mueller et al., 2006; Scroggs et al., 2009; Mirzaei et al., 2019). The sensitivity of the three herbicides of terbuthylazine, mesotrione, and nicosulfuron against water hardness was investigated, and it was found that terbuthylazine was significantly sensitive to water hardness, mesotrione showed no significant response, and nicosulfuron showed moderate sensitivity to the hardness of the sprayer tank water (Istvan & Endre, 2009).

One recommended solution to reduce the antagonistic effects of hard water on the absorption and translocation of herbicides is the use of adjuvants such as ammonium sulfate (AMS), the ability of which in resolving some herbicide incompatibilities with hard water is well-documented. AMS and ammonium nitrate have been reported to improve the absorption and efficacy of glyphosate (Maschhoff et al., 2000; Shaner et al., 2006; Pratt et al., 2003; Gauvrit, 2003; Faircloth et al., 2004; Nurse et al., 2008; Mirzaei et al., 2019; Soltani et al., 2011; Hajmohammadnia ghalibaf et al., 2015; Nosrati et al., 2012), glufosinate (Devkota & Johnson, 2016; Soltani et al., 2011; Maschhoff et al., 2000), mesotrione (Devkota & Johnson, 2016), sethoxydim (Matysiak & Nalewaja, 1999; Mirzaei et al., 2016), clethodim (Nandula et al., 2007), imazethapyr (Gronwald et al., 1993), thifensulfuron methyl and foramsulfuron (Bunting et al., 2004), penoxsulam (Pearson et al., 2008), nicosulfuron (Nalewaja & Matysiak, 2000; Hajmohammadnia ghalibaf et al., 2015), and 2,4-D (Devkota & Johnson, 2016; Patton et al., 2016; Roskamp et al., 2013) herbicides. The effect of the ammonium adjuvants varies according to the type of herbicide and plant species. Mirzaei et al. (2016, 2017, 2019) investigated the role of water hardness in the efficacy of 2,4-D, sethoxydim, and glyphosate herbicides for controlling *A. retroflexus*, *B. scoparia*, *Avena ludoviciana*, and *Phalaris minor* and the effects of adjuvants in overcoming the inhibitory effect of cations in the spray water on the efficacy of these herbicides. Their results showed that AMS was effective, but its impact was dependent on weed species. The effect was better in *A. retroflexus* than in *P. minor* or *A. ludoviciana*, and it was ineffective on *B. scoparia*. In three tested herbicides, the efficacy of AMS in overcoming the inhibitory properties of cations in 2,4-D and glyphosate was greater than that of sethoxydim.

Because the bedrock in Iran is comprised of lime and dolomite, an abundance of calcium and magnesium, occasionally in high concentrations, is found in water sources (Ahmadi, 1999). The current study was designed to determine the adverse effects of carrier water hardness on the performance of 2,4-D plus MCPA and mesosulfuron plus iodosulfuron plus mefenpyr-diethyl herbicides on wild mustard control in the greenhouse. The second objective was to evaluate the influence of adjuvants (AMS and urea ammonium nitrate (UAN)) in reducing these adverse effects.

Materials and methods

Plant material and culture

Wild mustard seeds were collected from 10 or more mature plants from infested fields around Tehran, Iran (35.6892 °N, 51.3890 °E) in 2018. They were sterilized with 5% sodium hypochlorite for 5 min and then rinsed with distilled water for 2 min. Fifty seeds were placed on a filter paper (Whatman #1) in 9-cm diameter Petri dishes. Seeds were floated in 2000 mg L^{-1} gibberellic acid for 24 h and then kept in Petri dishes containing moist filter paper for 3 days to break dormancy (Duran & Retamal, 1989; Hasanfard et al., 2021). Petri dishes with germinated seeds were placed into a growth chamber calibrated for a 26/18 °C day/night, 16-h photoperiod at 850 μmol^{-2} s^{-1} of light intensity and 60% relative humidity until transplanting (Gherekhloo et al., 2018). Eight germinated seedlings were planted at 1 cm depth in a 14 cm-diameter and 13 cm-height pot containing substrate with 40% clay, 40% sand, and 20% perlite to maintain soil moisture. Daily watering was done, and no fertilizer was applied. After emergence, seedlings were thinned to four similar plants per pot^{-1} at the two-leaf stage. The pots were placed in a greenhouse at 25 °C with a lighting period of 16 and 8 h of light and darkness, respectively.

Experiments and treatments

Each experiment was duplicated across two experimental runs with a ten-day interval between each other in August 2019. To prepare the treatments, hardness levels of 250, 500, 750, and 1000 mg L^{-1} were first obtained by adding different amounts of $CaCO_3$ salt to deionized water. The deionized water was also used as a soft water, 0 mg $CaCO_3$ L^{-1}, control. After dissolving the salt, adjuvant treatment including AMS or UAN was applied to the prepared solutions at three levels of 0, 1%, and 2% (w/v). Two herbicides, 2–4,D plus MCPA and mesosulfuron plus iodosulfuron plus mefenpyr-diethyl, were evaluated in separate experiments. 2–4,D plus MCPA herbicide (U46 combi fluid®, Gita Shimi Sahand, Iran, SL 67.5%) at five rates: 63.3, 126.6, 253.1, 506.3 and 1012.5 g a. i. ha^{-1}; and mesosulfuron plus iodosulfuron plus mefenpyr-diethyl herbicide (Atlantis®, Bayer CropScience, Germany, OD 12%) at five rates: 1.125, 2.25, 4.5, 9 and 18 g a. i. ha^{-1} were added to the prepared water solutions. Immediately after mixing, herbicides were applied to the 4–6-leaf stage weeds using a researcher-made moving boom sprayer (air pump sprayer) equipped with a TeeJet 8002 flat fan nozzle with a spraying width of 1 m (spray output rate of 187 L ha^{-1} at a pressure of 200 kPa).

Data collection and analysis

Three weeks after spraying, the above-ground live plants were cut from the soil surface, and their fresh weight was measured and used to calculate biomass. Experiments were conducted as a randomized complete block design in factorial arrangement with three replications and two runs. There was no significant difference between two time replications of each experiment ($p > 0.05$); therefore, data was pooled over experimental runs and averaged for analysis. The analysis of variance (ANOVA) was conducted using Minitab ver.18. Then, data was fitted and analyzed using a four-parameter log-logistic model developed by Ritz et al. (2015) (Eq. 1).

$$Y = c + \frac{d - c}{1 + e^{b(\log x - loge)}} \quad (1)$$

where Y is the fresh weight; d and c are upper and lower limits for Y, respectively; x is the dose of herbicide; e is the effective dose (g a. i. ha^{-1}) which is replaceable with any ED_{50}; and b is the slope of the curve around ED_{50}. The data was analyzed using Rstudio software, version 1.3.1056. The acceptability of the model at the 0.05 level of significance was not approved for all dose-response curves, because the F-test for lack-of-fit was significant. Therefore, data was fitted and analyzed using a three-parameter log-logistic model (Ritz et al., 2015; Eq. 2).

$$Y = \frac{d}{1 + e^{b(\log x - loge)}} \quad (2)$$

Box-Cox power transformation was conducted the drc package before fitting dose-response curves. ED_{50} was separated using 95% confidence intervals (CI).

Results

Performance of 2,4-D plus MCPA

Without a tank-mix of adjuvants (AMS or UAN), the carrier water hardness ($CaCO_3$ concentration) significantly influenced the performance of 2,4-D plus MCPA against wild mustard. The impacts varied depending on the concentration of $CaCO_3$ in the carrier water. The results showed that the ED_{50} values to fresh weight of wild mustard were significantly increased by the $CaCO_3$ concentration ≥ 500 mg L^{-1}, indicating a significant reduction in the performance of 2,4-D plus MCPA. When wild mustard plants were treated with carrier water containing 500, 750, and 1000 mg L^{-1} $CaCO_3$, 1.66-, 1.74-, and 1.83-fold increases in the ED_{50} values or a decrease in herbicide phytotoxicity were observed compared with the control (deionized water), respectively (Tables 1 and 2).

In the current experiment, adjuvants (AMS and UAN) applied as tank-mix in the carrier water were effective in decreasing the adverse effects of carrier water hardness on the performance of 2,4-D plus MCPA against wild mustard. The results showed that tank-mix application of AMS at 2% (w/v) led to a 1.60-fold decrease in the ED_{50} values or an increase in the herbicide performance compared with the control (no adjuvant) (Table 1).

The ranking of the adjuvants based on their performance in decreasing order for both ED_{50} in deionized water was UAN > AMS. With a tank-mix of AMS, ED_{50} values for 1% (w/v) were 265.28 and 290.14 g a. i. ha^{-1} for 250 and 1000 mg L^{-1} of $CaCO_3$, respectively. At 2% (w/v) AMS, these values were 156.66 and 214.98 g a. i. ha^{-1} for 250 and 1000 mg L^{-1} of $CaCO_3$, respectively. In neither of these levels were the obtained values significantly different (Table 1). Similarly, ED_{50} values for the tank-mix of 1% (w/v) UAN were 276.83 and 304.19 g a. i. ha^{-1} for 250 and 1000 mg L^{-1} of $CaCO_3$, respectively, which were not significantly different. Also, at 2% (w/v) UAN, they were 143.05 and 224.60 g a. i. ha^{-1} for 250 and 1000 mg L^{-1} of $CaCO_3$, respectively, which were significantly different (Table 2). The results showed that the tank-mix of AMS at 1% or 2% (w/v) to the carrier water containing hard water completely eliminated the adverse effects of water hardness on the phytotoxicity of 2,4-D plus MCPA against wild mustard.

Performance of Mesosulfuron plus Iodosulfuron plus Mefenpyr-diethyl

In the second experiment and without a tank-mix of adjuvants (AMS or UAN), unlike the first experiment, the treatment of mesosulfuron plus iodosulfuron plus mefenpyr-diethyl spray solution containing 250 to 1000 mg L^{-1} $CaCO_3$ on wild mustard had no significant effect on the ED_{50} values or herbicide performance (Tables 3 and 4).

However, the results showed that AMS and UAN applied as tank-mix in the carrier water were effective on the performance of mesosulfuron plus iodosulfuron plus mefenpyr-diethyl against wild mustard. The results showed that tank-mix application of AMS at 1% and 2% (w/v) led to a 1.39- and 1.86-fold decrease in ED_{50} values or an increase in the mesosulfuron plus iodosulfuron plus mefenpyr-diethyl performance compared with the control (no adjuvant) (Table 3).

Table 1 Estimated parameters from fitting log-logistic model to fresh weight response of wild mustard to 2,4-D plus MCPA at different concentration of $CaCO_3$ and ammonium sulfate application rates[a,b,c,d,e]

AMS % (w/v)	$CaCO_3$ concentration (mg L^{-1})	b (Slope)	SE	d (g pot $^{-1}$)	SE	ED_{50} (g a.i. ha^{-1})	SE	95% CI of ED_{50}	
0 (Control)	0 (deionized water)	1.42**	0.18	11.95**	0.47	232.38 b**	26.44	205.94	258.82
	250	1.84**	0.24	12.08**	0.43	246.38 b**	21.99	224.39	268.37
	500	1.31**	0.15	12.60**	0.41	386.31 a**	47.65	338.66	433.96
	750	1.03**	0.13	12.32**	0.44	406.11 a**	41.25	364.86	447.36
	1000	1.02**	0.12	12.43**	0.43	426.14 a**	56.82	369.32	482.96
1	0 (deionized water)	1.14**	0.12	12.27**	0.40	235.00 b**	27.65	207.35	262.65
	250	0.93**	0.10	12.79**	0.41	265.28 b**	24.43	240.85	289.71
	500	0.98**	0.11	12.14**	0.41	269.42 b**	29.39	240.03	298.81
	750	0.65**	0.09	12.11**	0.42	279.50 b**	39.37	240.13	318.87
	1000	0.84**	0.10	12.23**	0.41	290.14 b**	30.91	259.23	321.05
2	0 (deionized water)	1.51**	0.17	11.92**	0.40	145.23 c**	25.66	119.57	170.89
	250	1.01**	0.11	12.13**	0.41	156.66 c**	28.11	128.55	184.77
	500	0.78**	0.09	12.14**	0.41	169.56 c**	20.37	149.19	189.93
	750	1.04**	0.10	12.22**	0.40	177.15 c**	24.06	153.09	201.21
	1000	1.07**	0.10	12.32**	0.39	214.98 bc**	22.46	192.52	237.44

[a]*Abbreviation*: *AMS* Ammonium sulfate, *SE* Standard Error

[b]**: significant at $p \leq 0.01$

[c]ED_{50} were separated using it's 95% confidence intervals (CI) and those followed by same letter are not significantly different at at $p \leq 0.05$

[d]d is upper limits of the curves; the ED_{50} is the effective doses which caused 50% fresh weight reduction of wild mustard

[e]b is the slope of the curve around ED_{50}

The tank-mix application of UAN at 1% and 2% (w/v) resulted in 1.16- and 1.82-fold reductions in the ED_{50} values compared to the control (Table 4). Therefore, the adjuvants were similar in terms of their performance in decreasing order for ED_{50} of mesosulfuron plus iodosulfuron plus mefenpyr-diethyl in deionized water.

ED_{50} values for the tank-mix of 1% (w/v) AMS were 1.50 and 1.04 g a. i. ha^{-1} for 250 and 1000 mg L^{-1} of $CaCO_3$, respectively, which were not significantly different. At 2% (w/v) AMS, they were 1.24 and 0.59 g a. i. ha^{-1} for 250 and 1000 mg L^{-1} of $CaCO_3$, respectively, which were not significantly different in either concentration (Table 3). ED_{50} values for the tank-mix of 1% (w/v) UAN were 1.87 and 1.25 g a. i. ha^{-1} for 250 and 1000 mg L^{-1} of $CaCO_3$, respectively, which were not significantly different. However, at 2% (w/v), they were 1.40 and 1.07 g a. i. ha^{-1} for 250 and 1000 mg L^{-1} of $CaCO_3$, respectively, which were significantly different (Table 4).

For both herbicides evaluated in this research, the relationship between ED_{50} and $CaCO_3$ concentrations was linear. The slopes of these lines for 2,4-D plus MCPA were positive in the spray solution without adjuvants and near zero for the spray solution with AMS or UAN. The explanation is that the adjuvants, especially AMS at 1% and 2% (w/v), completely eliminated the adverse effect of water hardness on the phytotoxicity of 2,4-D plus MCPA against wild mustard (Fig. 1). Nonetheless, the slopes of these lines for mesosulfuron plus iodosulfuron plus mefenpyr-diethyl were negative in the spray solution with or without adjuvants (AMS and UAN). In other words, simultaneous with increasing water hardness, the ED_{50} values decreased or the performance of mesosulfuron plus iodosulfuron plus mefenpyr-diethyl increased. This result is especially true in the tank-mix of both adjuvants at all application rates (Fig. 2).

Discussion

The reduced efficacy of 2,4-D plus MCPA was attributed to Ca^{2+} cations, existing in the carrier water. 2,4-D dimethylamine salt is ionized in water into two anionic and cationic parts. In hard water, calcium,

Table 2 Estimated parameters from fitting log-logistic model to fresh weight response of wild mustard to 2,4-D plus MCPA at different concentration of $CaCO_3$ and urea ammonium nitrate application rates[a,b,c,d,e]

UAN % (w/v)	$CaCO_3$ concentration (mg L^{-1})	b (Slope)	SE	d (g pot $^{-1}$)	SE	ED_{50} (g a.i. ha^{-1})	SE	95% CI of ED_{50}	
0 (Control)	0 (deionized water)	1.42**	0.18	11.95**	0.47	232.38 b**	26.44	205.94	258.82
	250	1.84**	0.24	12.08**	0.43	246.38 b**	21.99	224.39	268.37
	500	1.31**	0.15	12.60**	0.41	386.31 a**	47.65	338.66	433.96
	750	1.03**	0.13	12.32**	0.44	406.11 a**	41.25	364.86	447.36
	1000	1.02**	0.12	12.43**	0.43	426.14 a**	56.82	369.32	482.96
1	0 (deionized water)	0.83**	0.08	12.15**	0.32	247.97 bc**	29.04	218.93	277.01
	250	0.61**	0.09	12.12**	0.32	276.83 b**	25.08	251.75	301.91
	500	0.41**	0.06	12.12**	0.32	283.37 b**	30.73	253.36	314.10
	750	0.58**	0.07	12.12**	0.32	299.32 b**	41.98	257.34	341.30
	1000	0.74**	0.09	12.19**	0.32	304.19 b**	32.21	271.98	336.40
2	0 (deionized water)	0.92**	0.18	12.03**	0.33	123.17 d**	25.82	97.35	148.99
	250	0.47**	0.08	12.12**	0.34	143.05 d**	29.80	113.25	172.85
	500	0.34**	0.06	12.14**	0.34	178.80 cd**	22.11	156.69	200.91
	750	0.77**	0.08	12.14**	0.34	187.53 cd**	26.21	161.32	213.74
	1000	0.78**	0.10	12.15**	0.33	224.60 c**	24.20	200.40	248.80

[a] *Abbreviation*: *UAN* Urea ammonium sulfate, *SE* Standard Error

[b] **: significant at $p \leq 0.01$

[c] ED_{50} were separated using it's 95% confidence intervals (CI) and those followed by same letter are not significantly different at at $p \leq 0.05$

[d] d is upper limits of the curves; the ED_{50} is the effective doses which caused 50% fresh weight reduction of wild mustard

[e] b is the slope of the curve around ED_{50}

magnesium, sodium cations, and iron bind to the anionic part and prevent its action. Studies have shown that a 350-mg L^{-1} concentration of calcium carbonate in water significantly reduces the efficiency of glyphosate in controlling grasses and broadleaved weeds (Altland, 2001). Increasing its concentration to 700 mg L^{-1} led to the inactivation of glyphosate, which required that the dose be increased (Altland, 2001). Christian (2003) reported that calcium ions in water could reduce the effect of glyphosate, where the presence of 250, 500, and 1000-mg L^{-1} calcium in the spray solution lowered the absorption of glyphosate by barley at 14%, 24%, and 48%, respectively. Izadi-Darbandi et al. (2011) reported the antagonistic effect of $CaCO_3$ on the efficacy of 2,4-D amine herbicide in controlling *A. retroflexus* L. and *Chenopodium album* L. and reduced the herbicide effects by increased water hardness. Devkota and Johnson (2019) illustrated that water hardness significantly affected dicamba efficacy for giant ragweed (*Ambrosia trifida* L.), palmer amaranth (*Amaranthus palmeri* (S.) Wats.), or pitted morning glory (*Ipomoea lacunosa* L.) control. Holm and Henry (2005) also reported that water containing $CaCO_3$ with concentrations higher than 500 mg L^{-1} reduced the performance of 2,4-D herbicide.

The tank-mix application of UAN at 2% (w/v) resulted in a 1.88-fold decrease in ED_{50} values compared to the control (Table 2). In other words, water hardness at 1000 mg L^{-1} reduced 2,4-D plus MCPA efficacy by 45%. Nalewaja and Matysiak (1993) showed that water hardness at 800 mg L^{-1} reduced dimethylamine dicamba efficacy by at least 50% for Kochia (*B. scoparia*) control.

In comparison, the addition of UAN at 1% or 2% (w/v) to the carrier containing hard water significantly reduced (but not completely eliminated) the adverse effect of carrier water hardness (especially 1000 mg L^{-1}) on the performance of 2,4-D plus MCPA against wild mustard. Hard water antagonism and the ability of AMS to overcome antagonism are well-documented with the weak-acid herbicide 2,4-D. AMS increases the uptake of the herbicide on the foliage, thereby increasing the herbicide's effectiveness. By adding AMS, the ammonium cation binds to the anion and prevents the binding of hard water cations,

Table 3 Estimated parameters from fitting log-logistic model to fresh weight response of wild mustard to mesosulfuron plus iodosulfuron plus mefenpyr-diethyl at different concentration of $CaCO_3$ and ammonium sulfate application rates [a,b,c,d,e]

AMS % (w/v)	$CaCO_3$ concentration (mg L^{-1})	b (Slope)	SE	d (g pot $^{-1}$)	SE	ED_{50} (g a.i. ha^{-1})	SE	95% CI of ED_{50}	
0 (Control)	0 (deionized water)	1.78**	0.22	12.19**	0.41	2.55a**	0.27	2.28	2.82
	250	1.51**	0.17	11.98**	0.42	2.25 a**	0.26	1.99	2.51
	500	1.72**	0.21	12.21**	0.41	2.19 a**	0.21	1.98	2.40
	750	1.39**	0.16	12.11**	0.42	2.10 a**	0.19	1.91	2.29
	1000	2.14**	0.30	12.19**	0.41	2.01 a**	0.16	1.85	2.17
1	0 (deionized water)	1.22**	0.19	12.11**	0.39	1.83 ab**	0.17	1.66	2.00
	250	1.33**	0.19	12.10**	0.39	1.50 b**	0.17	1.33	1.67
	500	1.58**	0.24	12.09**	0.39	1.37 bc**	0.16	1.21	1.53
	750	2.34**	0.48	12.19**	0.39	1.30 bc**	0.15	1.15	1.45
	1000	2.14**	0.49	12.17**	0.39	1.04 bc**	0.11	0.93	1.16
2	0 (deionized water)	0.94**	0.14	12.11**	0.38	1.37 bc**	0.20	1.17	1.57
	250	1.40**	0.19	12.11**	0.38	1.24 bc**	0.15	1.09	1.39
	500	1.37**	0.20	12.09**	0.38	1.03 bc**	0.16	0.87	1.19
	750	0.94**	0.13	12.11**	0.38	0.95 c**	0.20	0.75	1.15
	1000	0.84**	0.17	12.12**	0.38	0.59 c**	0.17	0.42	0.76

[a] *Abbreviation*: *AMS* Ammonium sulfate, *SE* Standard Error

[b] **: significant at $p \leq 0.01$

[c] ED_{50} were separated using it's 95% confidence intervals (CI) and those followed by same letter are not significantly different at at $p \leq 0.05$

[d] d is upper limits of the curves; the ED_{50} is the effective doses which caused 50% fresh weight reduction of wild mustard

[e] b is the slope of the curve around ED_{50}

and the herbicide acts naturally. Sobiech et al. (2020) reported that the application of adjuvants contributed to the reduction in the contact angle and the surface tension of spray droplets. Kochia injury from 2,4-D diethanolamine was reduced when applied in water containing either Ca, Mg, Na, and K salts, such that the antagonism could be overcome by adding AMS (Nalewaja et al., 1991). Similar to the current study results, Zollinger et al. (2010) illustrated that the use of AMS enhanced glufosinate efficacy in the presence of hard water cations. In another study, Nosrati et al. (2012) investigated the effects of adjuvants in overcoming the inhibitory effects of cations in the spray water on the performance of 2,4-D plus MCPA in controlling *G. glabra* L. The results showed that the effects of herbicide dose, adjuvants, and water quality of the sprayer tank on herbicide performance were highly significant.

A study by Roskamp et al. (2013) showed that the control of *C. album* is enhanced when AMS is added to the 2,4-D in the presence of the cations. This adjuvant does not affect the amine form of 2,4-D herbicide; thus, to overcome the antagonistic effects of hard water, it is necessary to use esteric or non-ionic surfactant 0.1%.

The increased herbicide activity with AMS was attributed to the improved herbicide movement through the leaf cuticle because of the ammonium ions present in AMS. Villiers et al. (2001) stated that sodium bicarbonate in water reduces tralkoxydim's performance on wild oats. They also showed that AMS and ammonium nitrate effectively increased the activity of this herbicide, while AMS was more effective than ammonium nitrate. They said that AMS overcame the antagonistic effects of calcium in the water and increased the uptake and transfer of herbicides to the plant. The pH of spraying water can negatively affect the efficacy of some herbicides. Green and Cahil (2003) showed that adding 2% AMS to the deionized water increased the spray solution pH from 4.6 to 4.7, leading to an increase in the nicosulfuron solubility from 12% to 16% and herbicide performance improvement in controlling *Digitaria sanguinalis*. It has been proven that even the addition

Table 4 Estimated parameters from fitting log-logistic model to fresh weight response of wild mustard to mesosulfuron plus iodosulfuron plus mefenpyr-diethyl at different concentration of $CaCO_3$ and urea ammonium nitrate application rates [a,b,c,d,e]

UAN % (w/v)	$CaCO_3$ concentration (mg L^{-1})	b (Slope)	SE	d (g pot $^{-1}$)	SE	ED_{50} (g a.i. ha^{-1})	SE	95% CI of ED_{50}	
0 (Control)	0 (deionized water)	1.78**	0.22	12.19**	0.41	2.55 a**	0.27	2.28	2.82
	250	1.51**	0.17	11.98**	0.42	2.25 a**	0.26	1.99	2.51
	500	1.72**	0.21	12.21**	0.41	2.19 a**	0.21	1.98	2.40
	750	1.39**	0.16	12.11**	0.42	2.10 a**	0.19	1.91	2.29
	1000	2.14**	0.30	12.19**	0.41	2.01 a**	0.16	1.85	2.17
1	0 (deionized water)	1.46**	0.16	12.18**	0.39	2.19 a**	0.15	2.04	2.34
	250	2.03**	0.22	12.22**	0.38	1.87 b**	0.15	1.72	2.02
	500	0.98**	0.11	12.10**	0.39	1.62 b**	0.18	1.44	1.80
	750	1.75**	0.24	12.19**	0.39	1.41 b**	0.13	1.28	1.54
	1000	0.95**	0.13	12.10**	0.39	1.25 b**	0.19	1.06	1.44
2	0 (deionized water)	1.37**	0.19	12.10**	0.39	1.40 b**	0.12	1.28	1.52
	250	1.19**	0.18	12.12**	0.39	1.40 b**	0.15	1.25	1.55
	500	1.50**	0.19	12.12**	0.39	1.28 b**	0.12	1.16	1.40
	750	1.57**	0.20	12.11**	0.39	1.12 bc**	0.14	0.98	1.56
	1000	1.96**	0.23	12.05**	0.39	1.07 c**	0.08	0.99	1.15

[a]*Abbreviation*: *UAN* Urea ammonium sulfate, *SE* Standard Error

[b]**: significant at $p \le 0.01$

[c]ED_{50} were separated using it's 95% confidence intervals and those followed by same letter are not significantly different at at $p \le 0.05$

[d]d is upper limits of the curves; the ED_{50} is the effective doses which caused 50% fresh weight reduction of wild mustard

[e]b is the slope of the curve around ED_{50}

of AMS to soft water in the spray tank increases the performance of glyphosate herbicide in *Abutilon theophrasti* and *Agropyron repense,* which have high calcium contents within their intercellular space (Hall et al., 1999). Nalewaja et al. (1989) reported the benefits of ammonium nitrate, AMS, and nitrogen liquid fertilizer in overcoming the adverse effects of sodium in controlling grasses in greenhouses and fields using sethoxydim herbicide. In this regard, in an experiment conducted by Hajmohammadnia Ghalibaf et al. (2015), ammonium nitrate overcame the negative effect of glyphosate and nicosulfuron herbicides by inhibiting sodium bicarbonate in the spray tank. Devkota and Johnson (2016) investigated the effects of hard water and AMS on the efficacy of glufosinate herbicide in controlling *Ambrosia* sp., *Conyza canadensis,* and *A. retroflexus* and indicated that hard water does not affect the efficacy of this herbicide on horseweed.

The presence of hardness cations in the spray water reduces the herbicide's solubility by binding to the anion of the herbicide molecules. The salt compound formed is not easily absorbed by the plant and will not have enough biological activity to control weeds. Overall, carrier water pH, hardness, co-applied foliar fertilizer, and use of AMS are critical considerations for obtaining optimum efficacy from herbicide application. According to Soltani et al. (2011), hard water has no adverse effect on the performance of glyphosate herbicide in controlling *C. album*, *Echinochloa crusgalli*, *Alopecurus pratensis*, *A. retroflexus*, *A. theophrasti*, and *Ambrosia* sp. Roskamp et al. (2013) also reported that the zinc cation in the spray solution does not affect the performance of 2,4-D herbicide in controlling redroot pigweed and horseweed. The effects of different salts in the hard water on herbicide performance vary depending on the cation type, herbicide type, and weed species (Nalewaja et al., 1989). As the morphophysiological characteristics of weeds are the most important factors affecting the performance of herbicides, this can result in varying tolerance levels of different weed species to herbicides (Holm & Henry, 2005). Also, the sensitivity

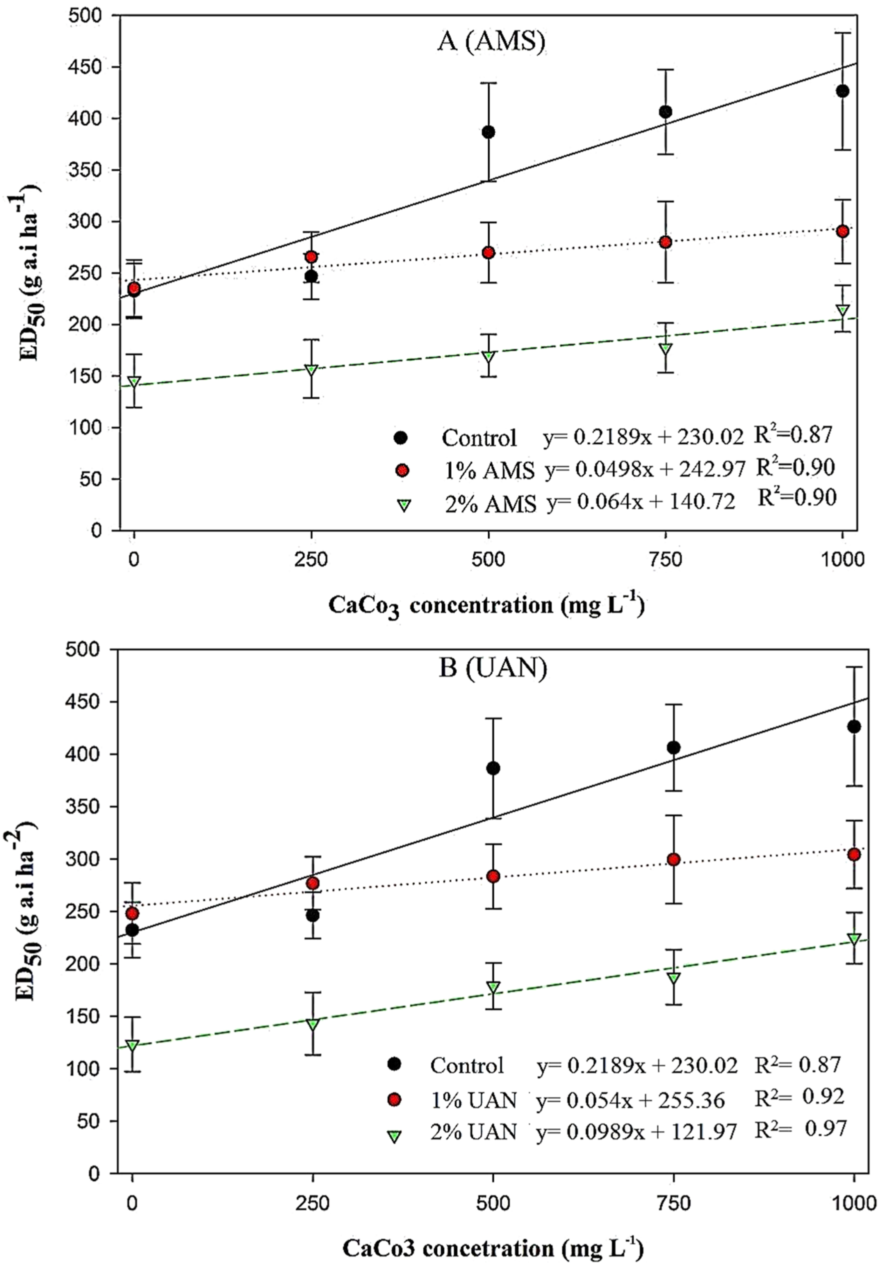

Fig. 1 Relationship between $CaCO_3$ concentration and ED_{50} of 2,4-D plus MCPA herbicide on wild mustard fresh weight at different ammonium sulfate (AMS) (**A**) and urea ammonium nitrate (UAN) (**B**) application rates (% w/v). Error bars represent Standard error (SE)

levels of herbicides to water hardness differ. Istvan and Endre (2009) investigated the sensitivity of three herbicides, terbuthylazine, mesotrione, and nicosulfuron, to water hardness. These researchers showed that terbuthylazine was significantly sensitive to water hardness, mesotrione had no significant response, and nicosulfuron herbicide performance was moderately altered with spray water hardness variations. These differences are mainly due to the differences in the chemical and physical structures of these herbicides, which affect their physicochemical properties. However, high concentrations of mineral salts eventually clog the spray nozzles, which reduces the uniformity of spraying. As such, herbicide spray performance is indirectly affected by water hardness, and weed control is not optimized.

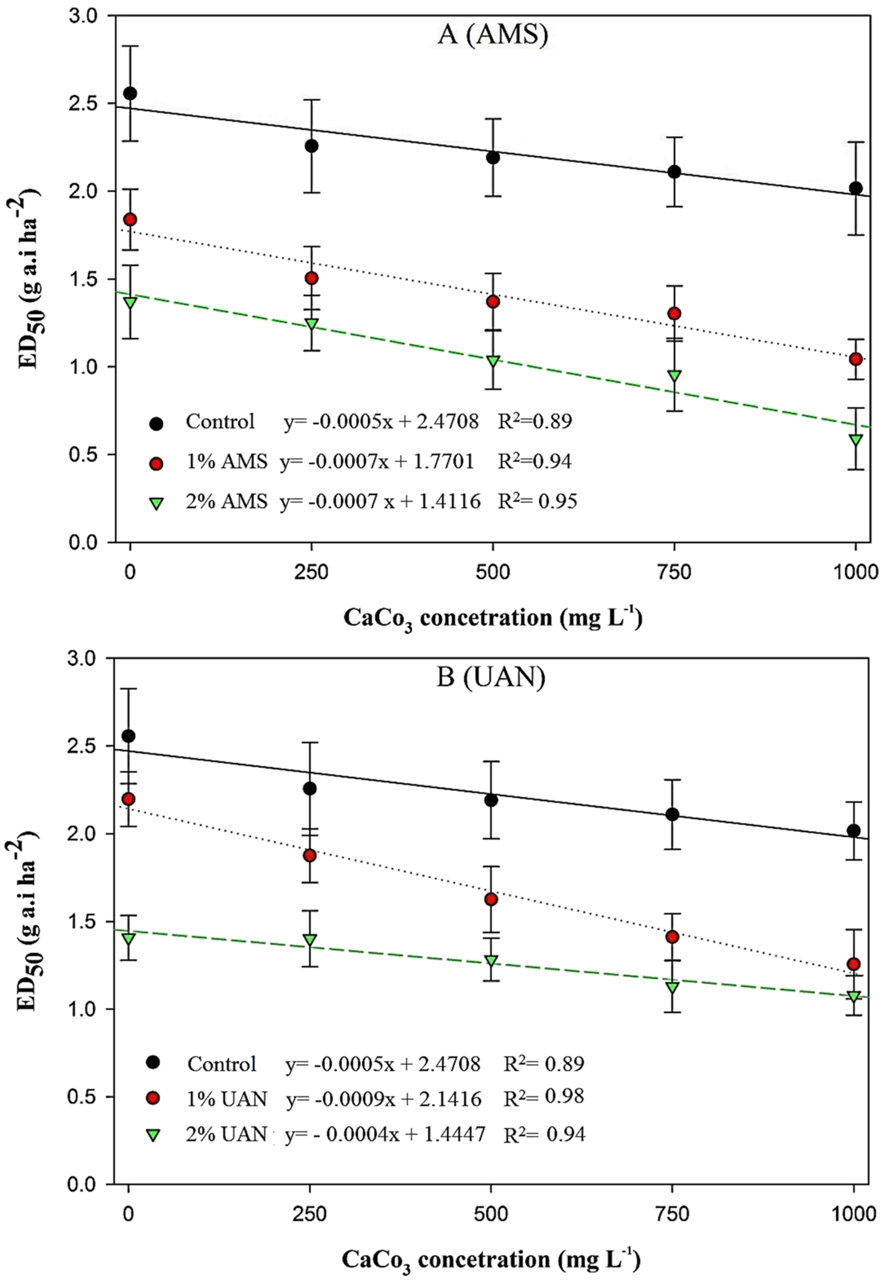

Fig. 2 Relationship between $CaCO_3$ concentration and ED_{50} of mesosulfuron plus iodosulfuron plus mefenpyr-diethyl herbicide on wild mustard fresh weight at different ammonium sulfate (AMS) (**A**) and urea nitrate ammonium nitrate (UAN) (**B**) application rates (% w/v). Error bars represent Standard error (SE)

Conclusion

The current research showed that water hardness led to a significant reduction in the performance of 2,4-D plus MCPA herbicide in controlling wild mustard. However, it had no significant effect on mesosulfuron plus iodosulfuron plus mefenpyr-diethyl herbicide performance in controlling that weed. The positive effects of AMS and UAN adjuvants in overcoming the negative effects of water hardness were observed. In 2,4-D plus MCPA herbicide, water hardness to 250 mg L^{-1} did not affect herbicide performance, while hardness at 500 mg L^{-1} or higher reduced the performance of 2,4-D plus MCPA. However, a tank-mix of 2% AMS and UAN increased the performance of 2,4-D plus MCPA herbicide. Mesosulfuron plus iodosulfuron plus mefenpyr-diethyl was not sensitive to water hardness; however, adding 2% (w/v)

AMS and 2% UAN adjuvants also increased herbicide performance. The results of the current study emphasized the importance of the spray water quality for herbicide application. This research also showed that the chemical and physical properties of the herbicides, type and amounts of adjuvants, and weed species should be considered for the maximum herbicide biological activity, and there is no general recommendation for increasing the performance of herbicides in controlling weeds in hard water. The findings of this study support the use of water-conditioning adjuvants such as AMS and UAN in tank mixtures to enhance the efficacy of 2,4-D plus MCPA and mesosulfuron plus iodosulfuron plus mefenpyr-diethyl.

Declarations

Conflict of interest The authors declare that there are no interests to declare.

References

Ahmadi, H. (1999). *Applied geomorphology (wind erosion)* (p. 688). Tehran University Press.

Altland, J. (2001). Water quality affects herbicide efficacy. http://www.oregonstate.edu. Accessed 11 Oct 2006.

Baily, W. A., Poston, D. H., Wilson, H. P., & Hines, T. E. (2002). Glyphosate interactions with manganese. *Weed Technology, 16*, 792–799.

Brown, K. (2006). Environmental impact on herbicide performance. *Manitoba Agriculture and Food.*, 440–443.

Bunting, J. A., Sprague, C. L., & Riechers, D. E. (2004). Proper adjuvant selection for foramsulfuron activity. *Crop Protection, 23*, 361–366.

Christian, G. (2003). Glyphosate response to calcium, ethoxylated amine surfactant, and ammonium sulfate. *Weed Technology, 17*, 799–804.

Devkota, P., & Johnson, W. G. (2016). Glufosinate efficacy as influenced by carrier water, hardness, foliar fertilizer and ammonium sulfate. *Weed Technology, 30*(4), 848–859.

Devkota, P., & Johnson, W. G. (2019). Influence of carrier water pH, foliar fertilizer, and ammonium sulfate on 2, 4-D and 2,4-D plus glyphosate efficacy. *Weed Technology, 33*, 562–568.

Devkota, P., Spaunhorst, D. J., & Johnson, W. G. (2016). Influence of carrier water pH, hardness, foliar fertilizer, and ammonium sulfate on mesotrione efficacy. *Weed Technology*, 617–628.

Duran, J. M., & Retamal, N. (1989). Coat structure and regulation of dormancy in *Sinapis arvensis* L. seeds. *Journal of Plant Physiology, 135*(2), 218–222.

Faircloth, W. H., Monks, C. D., & Patterson, M. G. (2004). Cotton and weed response to glyphosate applied with sulfur-containing additives. *Weed Technology, 18*, 404–411.

Gauvrit, C. (2003). Glyphosate response to calcium, ethoxylated amine surfactant, and ammonium sulfate. *Weed Technology, 17*, 799–804.

Gherekhloo, J., Hatami, Z., Alcántara-de la Cruz, R., Sadeghipour, H., & De Prado, R. (2018). Continuous use of Tribenuron-methyl selected for cross-resistance to Acetolactate synthase–inhibiting herbicides in wild mustard (*Sinapis arvensis*). *Weed Science, 66*(4), 424–432.

Green, J. M., & Cahil, W. R. (2003). Enhancing the biological activity of nicosulfuron with pH adjusters. *Weed Technology, 17*, 338–345.

Gronwald, J. W., Jourdan, S. W., Wyse, D. L., Somers, D. A., & Magnusson, M. U. (1993). Effect of ammonium sulfate on absorption of imazethapyr by quackgrass (*Elytrigia repens*) and maize (*Zea mays*) cell suspension cultures. *Weed Science, 41*, 325–334.

Hajmohammadnia ghalibaf, K., Rashed mohassel, M. H., Nassiri mahallati, M., & Zand, E. (2015). The influence of ammonium nitrate on antagonism of spray tank sodium bicarbonate on glyphosate and nicosulfuron performance on barnyard - grass and velvetleaf. *Journal of Plant Protection, 28*(3), 292–301.

Hall, G. J., Hart, C. A., & Jones, C. A. (1999). Twenty-five years of increasing glyphosate use: The opportunities ahead. *Pest Management Science, 56*, 351–358.

Han, H., Picoli, G. J., Jr., Guo, H., Yu, Q., & Powles, S. B. (2020). Mechanistic basis for synergism of 2,4-D amine and metribuzin in *Avena sterilis*. *Journal of Pest Science, 45*(4), 216–222.

Hasanfard, A., Rastgoo, M., Darbandi, E. I., Nezami, A., & Chauhan, B. S. (2021). Regeneration capacity after exposure to freezing in wild oat (*Avena ludoviciana* Durieu.) and turnipweed (*Rapistrum rugosum* (L.) All.) in comparison with winter wheat. *Environmental and Experimental Botany, 181*, 104271.

Holm, F.A., & Henry, J.L. (2005). Water quality and herbicides. Crop Science and Plant Ecology. http://www.gov.sk.ca. Accessed 11 Oct 2006.

Hsiao, A. I., Liu, S. H., & Quick, W. A. (1996). Effect of ammonium sulfate on the phytotoxicity, foliar uptake, and translocation of imazamethabenz in wild oat. *Plant Growth Regulation, 15*, 115–120.

Istvan, D., & Endre, M. (2009). Efficacy of herbicides influenced by spray carrier water pH and hardness. 5th International Plant Protection Symposium. Debrecen. pp. 141–146.

Izadi-Darbandi, E., Nessari, N., & Azarian, F. (2011). Investigation the effect of water hardness on 2,4-D amine efficacy on redroot pigweed (*Amaranthus retroflexous*) and common lambsquart (*Chenopodium album*) control. *Journal of Plant Protection, 25*, 258–265.

Maschhoff, J. R., Hart, S. E., & Baldwin, J. L. (2000). Effect of ammonium sulfate on the efficacy, absorption, and translocation of glufosinate. *Weed Science, 48*, 2–6.

Matysiak, R., & Nalewaja, J. D. (1999). Temperature, adjuvants, and UV light affect sethoxydim phytotoxicity. *Weed Technology, 13*, 94–99.

Mcmullan, P. (2000). Utility adjuvants. *Weed Technology, 14*, 792–797.

Mirzaei, M., Rastgoo, M., Hajmohammadnia Ghalibaf, K., & Zand, E. (2016). Efficiency study of sethoxidim in controlling little canarygrass (*Phalaris minor* Retz.) and winter wild oat (*Avena ludoviciana* Durieu) in presence of different salts and ammonium sulfate. *Weed Research Journal, 8*(1), 27–40.

Mirzaei, M., Rastgoo, M., Hajmohammadnia Ghalibaf, K., & Zand, E. (2017). Evaluation of the inhibitory effects of different salts on 2,4-d efficacy in control of Kochia (*Kochia scoparia* L.) and redroot pigweed (*Amaranthus retroflexus* L.). *Journal of Plant Protection, 31*(2), 267–276.

Mirzaei, M., Rastgoo, M., Hajmohammadnia Ghalibaf, K., & Zand, E. (2019). The response of different weed species to glyphosate using ammonium sulfate and hard water. *Planta Daninha, 37*. https://doi.org/10.1590/S0100-83582019370100041

Mueller, T. C., Main, C. L., Thompson, M. A., & Steckel, L. E. (2006). Comparison of glyphosate salts (isopropylamine, diammonium, and potassium) and calcium and magnesium concentrations on the control of various weeds. *Weed Technology, 20*, 164–171.

Nalewaja, J. D., & Matysiak, R. (1991). Salt antagonism of glyphosate. *Weed Science, 39*, 622–628.

Nalewaja, J. D., & Matysiak, R. (1993). Spray carrier salts affect herbicide toxicity to Kochia (*Kochia scoparia*). *Weed Technology, 7*, 154–158.

Nalewaja, J. D., & Matysiak, R. (2000). Spray deposits from nicosulfuron with salts that affect efficacy. *Weed Technology, 14*, 740–749.

Nalewaja, J. D., Manthey, F. A., Szelezniak, E. F., & Anyska, A. (1989). Sodium bicarbonate antagonism of sethoxydim. *Weed Technology, 3*, 654–658.

Nalewaja, J. D., Woznica, Z., & Matysiak, R. (1991). 2,4-D amine antagonism by salts. *Weed Technology, Champaign, 5*, 873–880.

Nandula, V. K., Poston, D. H., Reddy, K. N., & Koger, C. H. (2007). Formulation and adjuvant effects on uptake and translocation of clethodim in bermudagrass (*Cynodon dactylon*). *Weed Science, 55*, 6–11.

Naylor, R. E. L. (2002). *Weed Management Handbook* (Ed. 9). John Wiley and Sons.

Nosrati, I., Alizadeh, H., & Rahimian Mashhadi, H. (2012). Effect of some adjuvants on overcoming antagonistic effects of spray carrier water quality on glyphosate and herbicide mixture 2,4-D+MCPA efficacy on licorice (*Glycyrrhiza glabra*). *Iranian Journal ofWeed Science, 7*(2), 49–60.

Nurse, R. E., Hamill, A. S., Kells, J. J., & Sikkema, P. H. (2008). Anuual wed control may be improved when AMS is added to below-label glyphosate doses in glyphosate-tolerant maize (*Zea mays* L.). *Crop Protection, 27*, 452–458.

Patton, A. J., Weisenberger, D. V., & Johnson, W. G. (2016). Divalent cations in spray water in fluence 2,4-D efficacy of dandelion (*Taraxacum officinale*) and broadleaf plantain (*Plantago major*). *Weed Technology, 30*, 431–440.

Pearson, B. A., Scott, R. C., & Carey, V. F. (2008). Urea ammonium nitrate effects on bispyribac and penoxsulam efficacy. *Weed Technology, 22*, 597–601.

Penner, D. (2006). Novel water conditioning agents for glyphosate. In North Central Weed Science Society Proceedings (Vol. 61, p. 150).

Petroff, R. (2000). Water quality and pesticide performance. http://scarab.msu.montana.edu. Accessed 11 Oct 2006.

Pratt, D., Kells, J. J., & Penner, D. (2003). Substitutes for ammonium sulfate as additives with glyphosate and glufosinate. *Weed Technology, 17*, 576–581.

Ritz, C., Baty, F., Streibig, J. C., & Gerhard, D. (2015). Dose-response analysis using R. *PLoS One, 10*(12), e0146021.

Roskamp, J. M., Chahal, G. S., & Johnson, W. G. (2013). The effect of cations and ammonium sulfate on the efficacy of dicamba and 2,4-D. *Weed Technology, 27*, 72–77.

Scroggs, D. M., Miller, D. K., Stewart, A. M., Leonard, B. R., Griffin, J. L., & Blouin, D. C. (2009). Weed response to foliar coapplications of glyphosate and zinc sulphate. *Weed Technology, 23*, 171–174.

Shahbazi, S., Diyanat, M., Mahdavi, S., & Samadi, S. (2019). Broadleaf weed control in rain-fed chickpea. *Weed Technology, 33*, 727–732.

Shaner, D. L., Westra, P., & Nissen, S. (2006). AMADS increases the efficacy of glyphosate formulations on corn. *Weed Technology, 20*, 179–183.

Singh, A., Mahajan, G., & Chauhan, B. S. (2022). Germination ecology of wild mustard (*Sinapis arvensis*) and its implications for weed management. *Weed Science, 70*(1), 103–111.

Siyahpoosh, A., Fathi, G., Zand, E., Siadat, S., Bakhshande, A., & Gharineh, M. H. (2012). Competitiveness of different densities of two wheat cultivars with wild mustard weed species (*Sinapis arvensis* L.) in different densities. *World Applied Sciences Journal, 20*(5), 748–752.

Sobiech, L., Grzanka, M., Skrzypczak, G., Idziak, R., Włodarczak, S., & Ochowiak, M. (2020). Effect of adjuvants and pH adjuster on the efficacy of sulcotrione herbicide. *Agronomy, 10*(4), 530.

Soltani, N., Nurse, R. E., & Sikkema, P. H. (2011). Effect of ammonium sulfate and water hardness on glyphosate and glyphosinate activity in corn. *Canadian Journal of Plant Science, 91*, 1053–1059.

Thelen, K. D., Jackson, E. P., & Penner, D. (1995). The basis for the hard-water antagonism of glyphosate activity. *Weed Science, 43*, 541–548.

Villiers, B. L. D., Kudsk, P., Smit, J. J., & Mathiassen, S. K. (2001). Tralkoxydim adjuvant, MCPA and other effects. *Weed Research, 41*, 547–556.

Zollinger, R. K., Nalewaja, J. D., Peterson, D. E., & Young, B. G. (2010). Effect of hard water and ammonium sulfate on weak acid herbicide activity. *Journal of ASTM International, 7*, 1–10.