Spray water quality and herbicide performance: a review

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Abstract

Water is the primary carrier for herbicide applications. Spray water qualities such as pH, hardness, temperature, or turbidity can influence herbicide performance and may need to be amended for optimum weed control. Water quality factors can affect herbicide activity by reducing solubility, enhancing degradation in the spray tank, or forming herbicide-salt complexes with mineral cations, thereby reducing the absorption, translocation, and subsequent weed control. The available literature suggests that the effect of water quality varies with herbicide chemistry and weed species. The efficacy of weak-acid herbicides such as glyphosate, glufosinate, clethodim, sethoxydim, bentazon, and 2,4-D is improved with acidic water pH; however, the efficacy of sulfonylurea herbicides is negatively impacted. Hard-water antagonism is more prevalent with weak-acid herbicides, and trivalent cations are the most problematic. Spray solution temperature between 18 C and 44 C is optimum for some weak-acid herbicides; however, their efficacy can be reduced at relatively low (5 C) or high (56 C) water temperature. The effect of water turbidity is severe on cationic herbicides such as paraquat and diquat, and herbicides with low soil mobility such as glyphosate. Although adjuvants are recommended to overcome the negative effect of spray water hardness or pH, the response has been inconsistent with the herbicide chemistry and weed species. Moreover, information on the effect of spray water quality on various herbicide chemistries, weed species, and adjuvants is limited; therefore, it is difficult to develop guidelines for improving weed control efficacy. Further research is needed to determine the effect of spray water factors and develop specific recommendations for improving herbicide efficacy on problematic weed species.

Introduction

Herbicides are the primary method of weed control in agronomic crops and contribute significantly to increased crop yield and global food security. Chemical weed control relies on synthetic, organic herbicides that fall into several different mode of action groups (Loux et al. 2014). Herbicide application at the proper timing, rate, and carrier volume is critically necessary for effective weed control (Foster et al. 1993; Mallory-Smith and Retzinger 2003). Despite the widespread use of herbicides, weeds still cause considerable economic losses, with about US$8 billion annually in the United States (Loux et al. 2014). Effective weed control also depends on the interaction of herbicide molecules with water quality factors that can influence efficacy (Aladesanwa and Oladimeji 2005; Devkota et al. 2016a, 2016b; Roskamp et al. 2013a).

Herbicides are formulated as concentrated products to facilitate handling, transportation, storage, mixing, and application (Tominack and Tominack 2000). Water is the predominant carrier solvent directly used for herbicide application and spray deposition on targeted weeds. Water is an optimum solvent for spray application, enabling the uniform distribution of a small quantity of herbicide product over a large area. Likewise, water is a polar molecule, which allows it to interact with many hydrophilic herbicides without solubility concern. Adhesion is another important property because water can stick to other surfaces such as leaves, and stems, which helps the herbicide to spread on the plant surface. In most cases, water comprises more than 99% of the spray mixture, which makes it an indispensable component for herbicide application and can have a significant effect on optimizing weed control efficacy (Devkota et al. 2016b).

Water quality factors such as pH, hardness, temperature, turbidity, and the concentration of polyvalent cations, can influence herbicide performance (Buhler and Burnside 1983; Devkota et al. 2016a, 2016b; Johnson and Young 2002; Roskamp et al. 2013a). With the increased cases of herbicide-resistant weeds, it is essential to understand the effects of spray water quality on herbicide performance to optimize the spray mixture for effective weed control. Various research

studies have evaluated the effect of spray water quality factors on herbicide efficacy, but the information has yet to be presented in a single document. This review article aims to compile existing literature and provide an overview of the influence of spray water quality on herbicide performance and the underlining mechanisms deriving such effects. In addition, strategies to mitigate the adverse effects of spray water quality are presented.

Effect of Spray Water Quality on Herbicide Performance

Water used for herbicide application is obtained from above-ground (streams, ponds, canals, reservoirs, or lakes) and underground (shallow domestic wells or deep underground aquifers) sources (Deepali et al. 2011). These water sources differ in characteristics such as pH, concentration of cations, turbidity, hardness, presence of carbonates and bicarbonates, and temperature, depending on the geographical location (Chahal et al. 2012; Coes et al. 2015). The inconsistencies in water quality factors could result in differences in herbicide performance through various mechanisms.

Spray Water pH and Herbicide Performance

Spray water pH is one of the most critical water quality factors influencing herbicide performance (Roskamp et al. 2013a). Acidic or alkaline spray water pH can adversely affect herbicide efficacy by affecting the solubility, hydrolysis, dissociation, or chemical breakdown of the herbicide molecule (Green and Hale 2005; Roskamp and Johnson 2013; Sarmah and Sabadie 2002). A lower- or higher-than-optimal water pH may result in reduced solubility or rapid dissociation of active herbicide ingredient into an inactive degradative product, which subsequently affects the herbicide absorption and translocation (Green and Cahill 2003; Grzanka et al. 2021; Roskamp et al. 2013a).

The influence of spray water pH on hydrolysis and resulting efficacy depends on herbicide chemistry and targeted weed species. In acidic spray water (pH <7), the sulfonylurea herbicides such as prosulfuron, primisulfuron, rimsulfuron, nicosulfuron, chlorimuron, chlorsulfuron, trifloxysulfuron, thifensulfuron-methyl, and metsulfuron-methyl hydrolyzed more rapidly to non-herbicidal molecules than in neutral water pH (Berger and Wolfe 1996; Green and Cahill 2003; Green and Hale 2005; Matocha and Sensemen 2007; Sarmah and Sabadie 2002). There was no difference in the rate of hydrolysis between alkaline and neutral pH (Green and Cahill 2003; Green and Hale 2005; Matocha and Sensemen 2007; Sarmah and Sabadie 2002). The active molecule of trifloxysulfuron was degraded by 10% in about 48 h after mixing in acidic water, while it required more than 120 h for an equivalent degradation in neutral or alkaline water (Matocha and Senseman 2007). This indicates that trifloxysulfuron is more stable and degrades less in spray water with alkaline pH, leading to greater absorption and translocation (Sarmah and Sabadie 2002). Matocha et al. (2006) demonstrated that the absorption of ^{14}C-trifloxysulfuron on Palmer amaranth (*Amaranthus palmeri* S. Watson) and Texasweed (*Caperonia palustris* L.) was 15% greater when applied with carrier water 9 compared with pH 5. Additionally, the study by Matocha et al. (2006) showed that the higher absorption of ^{14}C-trifloxysulfuron at pH 9 translated into greater ^{14}C-trifloxysulfuron translocation, indicating a potential for increased efficacy at alkaline spray water pH. Nicosulfuron also showed greater activity on common cocklebur (*Xanthium strumarium* L.) and large crabgrass (*Digitaria sanguinalis* L.) at alkaline compared to acidic water pH (Green and Cahill 2003).

Similarly, the efficacy of saflufenacil on giant ragweed, common lambsquarters (*Chenopodium album* L.), and field corn (*Zea mays* L) was greater by 56% when applied with spray solution at pH 7.7 compared to pH 4.0 (Roskamp et al. 2013a).

The reduction in the efficacy of trifloxysulfuron, nicosulfuron, and saflufenacil at low or acidic spray water pH may be due to reduced solubility of the herbicides. Water solubility of the sulfonylurea herbicides is directly related to the acid dissociation (pKa) constant (Table 1), which ranges from 3.3 to 5.2 (Sarmah and Sabadie 2002; Senseman 2007; Shaner 2014). Previous studies have shown that herbicide solubility is low when the spray solution pH is below the pKa constant, and the herbicides are not ionized but form dispersions and precipitates (Sarmah and Sabadie 2002; Senseman 2007). This could negatively affect the absorption and subsequent translocation of the herbicide molecules on targeted plants (Green and Cahill 2003; Matocha et al. 2006; Roskamp et al. 2013a). For example, when nicosulfuron solubility was reduced at acidic spray water pH, control of large crabgrass was reduced by 40% (Green and Cahill 2003). The reduction in absorption has been reported for herbicides that form precipitates or crystals on the leaf surface (Nalewaja and Matysiak 2000). Generally, the solubility of sulfonylurea herbicides is increased, and weed control is improved at neutral or alkaline pH (Sarmah and Sabadie 2002; Senseman 2007).

For herbicides such as mesotrione, tembotrione, sulcotrione, and bipyrazone that inhibit 4-hydroxyphenylpyruvate dioxygenase (HPPD), improved efficacy has been reported with acidic or alkaline spray water pH; however, the response was variable with the weed species (Grzanka et al. 2021; Sobiech et al. 2018, 2019, 2020). The efficacy of mesotrione on horseweed increased with acidic compared to alkaline spray water (Devkota et al. 2016a). In contrast, mesotrione efficacy was greater with alkaline compared to acidic spray water for barnyardgrass [*Echinochloa crus-galli* (L.) Beauv.; Sobiech et al. 2018]. Variation in results may be attributed to the differences in the leaf morphological characteristics (cuticle, trichomes, etc.) among the weed species, and potential for crystalline salt formation (Hall et al. 2000; Harr et al. 1991; Liu et al. 2004). For instance, the epicuticle wax content for barnyardgrass was reported at 19 µg cm^{-2} (Sanyal et al. 2006) but varied between 1 to 80 µg cm^{-2} for horseweed (Koger and Reddy 2005). Such differences can result in variations in herbicide penetration and lead to inconsistent weed control activity.

Although the water solubility of weak-acid herbicides is generally low at acidic compared to alkaline water pH (Table 1), the uptake through the leaf cuticle is greater in acidic compared to alkaline water pH for weak-acid herbicides such as clethodim, sethoxydim, bentazon, glyphosate, glufosinate, and 2,4-D (Matocha et al. 2006; Muir and Hansch 1955). This is because the pKa's of the functional weak-acid groups range between 1 and 7, and at pH below the pKa, the functional group will mostly be protonated, non-ionic, and diffuse readily into the plant cuticle (Green and Hale 2005). When the spray water pH is below the herbicide pKa, and solubility is a limiting factor for herbicide uptake, increasing pH can increase solubility. However, when solubility is not a limiting factor, and the pH is raised above the pKa, weak-acid herbicides become ionic, and thus penetration through the lipophilic cuticle, negatively charged cell wall, and membrane is reduced (Green and Hale 2005; Nalewaja et al. 1991; Stirling 1994). Ruiz and Ortiz (2005) reported reduced glyphosate efficacy on broadleaf signalgrass (*Brachiaria extensa* L.) with an alkaline compared to acidic spray water pH. Similar results were observed for glyphosate efficacy on palisade grass (*Brachiaria brizantha* L.;

Table 1. Mode of action, acid dissociation constant, and water solubility of the herbicides mentioned in the review[a]

Herbicide	Mode of action	pKa	Water solubility	References
2,4-D	Synthetic auxin	2.8, weak acid	900 mg L^{-1} (25 C)	Wauchope et al. (1992)
Atrazine	Photosystem II inhibitor	1.7 (21 C), weak base	33 mg L^{-1} (pH 7, 22 C)	LeBaron and Gressel (1982); Wauchope et al. (1992)
Chlorimuron	ALS inhibitor	4.2, weak acid	11 mg L^{-1} (pH 5, 25 C); 450 mg L^{-1} (pH 6.5, 20 C); 1,200 mg L^{-1} (pH 7, 20 C)	Senseman (2007); Wauchope et al. (1992)
Chlorsulfuron	ALS inhibitor	3.6 (25 C)	587 mg L^{-1} (pH 5); 31,800 mg L^{-1} (pH 7)	Senseman (2007); Wauchope et al. (1992)
Clodinafop	ACCase inhibitor	2.91, weak acid	4.0 mg L^{-1} (pH 7, 25 C)	Senseman (2007)
Cyhalofop	ACCase inhibitor	NA	0.44 mg L^{-1} (pH 7, 20 C)	Wauchope et al. (1992)
Dicamba	Synthetic auxin	1.87, weak acid	4,500 mg L^{-1} (25 C)	Wauchope et al. (1992)
Diclosulam	ALS inhibitor	4.09 (20 C), weak acid	117 mg L^{-1} (pH 5, 20 C); 124 mg L^{-1} (pH 7, 20 C); 4,290 mg L^{-1} (pH 9, 20 C)	Wauchope et al. (1992); Senseman (2007)
Diflufenzopyr	Auxin transport inhibitor	3.18, weak acid	270 mg L^{-1} (pH 5); 5,850 mg L^{-1} (pH 7); 10,546 mg L^{-1} (pH 9)	Wauchope et al. (1992)
Diquat	Photosystem I inhibitor	None, non-ionizable	718,000 mg L^{-1} (pH 7.2, 20 C)	Senseman (2007); Wauchope et al. (1992)
Endothall	Not classified	3.4 and 6.7	100 g L^{-1} (pH 7, 25 C)	Senseman (2007); Wauchope et al. (1992)
Fomesafen	PPO or Protox inhibitor	2.7 (20 C), weak acid	50 mg L^{-1} (pH 7, 25 C) <1 mg L^{-1} (pH 1, 25 C)	Colby et al. (1983); Duke et al. (1991)
Glufosinate	Glutamine synthetase inhibitor	<2, 2.9, and 9.8	1,370,000 mg L^{-1} (pH 7, 20 C);	Wauchope et al. (1992)
Glyphosate	EPSPS inhibitor	Acid 2.6, 5.6, 10.3	15,700 mg L^{-1} (pH 7, 25 C); 11,600 mg L^{-1} (pH 2.5, 25 C)	Wauchope et al. (1992); Senseman (2007); Duke and Hoagland (1978)
Imazethapyr	ALS inhibitor	2.1 and 3.9, weak acid	1,400 mg L^{-1} (pH 7, 25 C)	Senseman (2007); Shaner and O'Connor (1991)
Isoxaflutole	Carotenoid biosynthesis inhibitor	None, non-ionizable	6.8 mg L^{-1} (pH 5); 6.2 mg L^{-1} (pH 5.5) decompose at pH 9	European Commission (2003); Senseman (2007)
Mesotrione	Carotenoid biosynthesis inhibitor	3.12, weak acid	2,200 mg L^{-1} (pH 4.8, 20 C); 15,000 mg L^{-1} (pH 6.9 20 C); 22,000 mg L^{-1} (pH 9, 20 C)	European Commission (2003); Luscombe et al. (1995)
Metsulfuron-methyl	ALS inhibitor	3.3, weak acid	548 mg L^{-1} (pH 9, 25 C); 2,790 mg L^{-1} (pH 7, 25 C); 213,000 mg L^{-1} (pH 9, 25 C)	Senseman (2007); Wauchope et al. (1992)
Nicosulfuron	ALS inhibitor	4.3, weak acid	0.04% (pH 5); 0.018 (pH 7); 0.0068 (pH 9)	Augustijn-Beckers et al. (1994); Senseman (2007)
Primisulfuron	ALS inhibitor	5.1, weak acid	3.3 mg L^{-1} (pH 5, 20 C) 243 mg L^{-1} (pH 7, 20 C0 5,280 mg L^{-1} pH 9, 20 C)	Augustijn-Beckers et al. (1994); Senseman (2007)
Prosulfuron	ALS inhibitor	3.74, weak acid	30 mg L^{-1} (pH 5.1, 20 C); (pH 6.8, 20 C) 3,580 mg L^{-1}	Senseman (2007)
Rimsulfuron	ALS inhibitor	4.1	<10 mg L^{-1} unbuffered distilled water; 7,300 mg L^{-1} in buffered pH 7.0 water	Palm et al. (1989); Senseman (2007)
Sethoxydim	ACCase inhibitor	4.16, weak acid	257 mg L^{-1} (25 C, pH 5); 4,390 mg L^{-1} (25 C, pH 7)	Campbell and Penner (1985)
Simazine	Photosystem II inhibitor	1.62, weak acid	2 mg L^{-1} mg L^{-1} (0 C); 3.5 (20 C); 6.3 mg L^{-1} L (22 C); 84 mg L^{-1}	Senseman (2007); Wauchope et al. (1992)
Tralkoxydim	ACCase inhibitor	4.3, weak acid	6 mg L^{-1} (20 C pH 5); 6.7 mg L^{-1} (20 C pH 6.5) 8,850 mg L^{-1} (20 C pH 9)	Senseman (2007); Wauchope et al. (1992)
Trifloxysulfuron-methyl	ALS inhibitor	4.4, weak acid	1 mg L^{-1} (pH 3, 25 C); 3 mg L^{-1} (pH 5, 25 C) 110 mg L^{-1} (pH 7, 25 C); 11,000 mg L^{-1} (pH 9, 25 C)	Senseman (2007)
Quizalofop-p	ACCase inhibitor	1.25, weak acid	0.3 mg L^{-1} (20 C)	Senseman (2007)

[a]Abbreviatons: ACCase, acetyl co-enzyme A carboxylase; ALS, acetolactate synthase; EPSPS, 5-enolpyruvylshikimate 3-phosphate synthase; pKa, acid dissociation constant; PPO, protoporphyrinogen oxidase.

Dan et al. 2009). Glufosinate efficacy on Palmer amaranth and giant ragweed was reduced by 10% to 12% at spray water pH 9 compared to spray water pH 4 (Devkota and Johnson 2016a). The reduced efficacy of these herbicides at alkaline spray water pH was attributed to the dissociation of the herbicide molecules when dissolved in alkaline water, which could have resulted in lower accumulation in the plant and reduced effectiveness (Dan et al. 2009; Matocha et al. 2006). Conversely, increased efficacy at acidic spray water pH was attributed to a higher proportion of the herbicide molecules in an undissociated form that can easily diffuse through the leaf cuticle (Liu 2002; Devkota and Johnson 2016a).

Spray Water Hardness and Herbicide Performance
Herbicide spray mixtures are prepared with water from various sources, which may consist of high levels of cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), iron (Fe^{2+} or Fe^{3+}), aluminum (Al^{3+}), zinc (Zn^{2+}), and manganese (Mn^{2+}). The divalent and polyvalent

charges of these cations can bind efficiently to the negatively charged herbicide molecules and form a less soluble or inactive herbicide-salt complex, which is not readily absorbed and translocated in the plant (Bailey et al. 2002; Roskamp et al. 2013b). Furthermore, interaction of herbicide molecules and cations can increase the spray droplet size, resulting in less retention and reduced uptake of the active ingredient (Hoffmann et al. 2011).

The presence of hard water cations in the spray mixture can have a negative effect on herbicide efficacy. Several researchers have reported hard water antagonism on weak-acid herbicides such as sethoxydim (Matysiak and Nalewaja 1999); clethodim and tralkoxydim (De Villiers et al. 2001); aminopyralid, diflufenzopyr, dicamba, and tembotrione (Zollinger et al. 2011); 2,4-D (Roskamp et al. 2013b; Schortgen and Patton 2021; Zollinger et al. 2010); MCPA amine and glufosinate (Zollinger et al. 2010; Devkota and Johnson 2016a); imazethapyr (Aliverdi et al. 2014; Gronwald et al. 1993); paraquat and diquat (Zollinger et al. 2010); and glyphosate (Bailey et al. 2002; Bernards et al. 2005; Nalewaja and Matysiak 1991; Zollinger et al. 2010). These studies indicate that the impact of hard water cations on herbicide performance is often related to the cation, herbicide, and weed species. Studies have shown that trivalent cations such as Al^{3+} and Fe^{3+} result in a greater negative effect on glyphosate activity than monovalent and divalent cations (Bernards et al. 2005; Nalewaja and Matysiak 1991). A few studies have reported that Fe^{3+} cation resulted in greater antagonism on glyphosate than divalent cations (Stahlman and Phillips 1979; Sundaram and Sundaram 1997). Furthermore, a higher chelation constant is reported for methylglyphosate with Fe^{3+} than with Mn^{2+}, which results in a very stable glyphosate-Fe^{3+} complex in the solution (Motekaitis and Martell 1985). Bernards et al. (2005) reported that there was a rapid absorption of glyphosate-Fe^{3+} complex into the treated leaf; however, it bound tightly in the apoplast, reducing further translocation.

Glyphosate is the most widely studied herbicide with hard water antagonism, and most of the studies have reported a reduction in efficacy with the presence of hard water cations (Abouziena et al. 2009; Chahal et al. 2012; Devkota et al. 2016a; Hall et al. 2000; Mueller et al. 2006; Pratt et al. 2003). The presence of Ca^{2+}, Mg^{2+}, and Zn^{2+} in the spray water reduced glyphosate efficacy on velvetleaf (Abutilon theophrasti L.), barnyard grass, and yellow nutsedge (Cyperus esculentus L.; Abouziena et al. 2009; Hall et al. 2000). Mueller et al. (2006) reported that presence of Mg^{2+} in spray water reduced glyphosate efficacy on broadleaf signalgrass, pitted morningglory, Palmer amaranth, and yellow nutsedge. This result was attributed to the formation of glyphosate-magnesium complex and inactivation of isopropylamine in glyphosate molecules, thereby reducing plant uptake. A nuclear magnetic resonance analysis of the effect of Ca^{2+} and Mg^{2+} on isopropylamine formulation of ^{14}C-glyphosate demonstrated inactivation of isopropylamine through the formation of a less readily absorbed calcium-glyphosate and magnesium-glyphosate conjugate salt with the phosphate and carboxylic groups of glyphosate molecule, thereby reducing herbicide efficacy (Thelen et al. 1995).

Glyphosate activity was reduced on velvetleaf, common lambsquarters, giant foxtail (Setaria faberi Herrm.), smooth pigweed (Amaranthus hybridus L.), and large crabgrass (Digitaria sanguinalis L.) due to the presence of Mn^{2+} in the spray water (Bernards et al. 2005). In a similar study, Bailey et al. (2002) reported that the antagonistic effect might be due to the chelation of glyphosate molecules with cations, which led to the precipitation of the herbicide from the solution and limited the penetration of

the herbicide through the leaf cuticle. However, Bernards et al. (2005) suggested that the effect of Mn^{2+} antagonism on glyphosate efficacy is not only limited to reactions in the spray tank or leaf surface but also in the cytoplasm, where glyphosate may form a complex with Mn^{2+} and result in lower efficacy. According to Caetano et al. (2012), the formation of herbicide-cation complexes with Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, and Fe^{3+} could prevent glyphosate from binding to the enzyme 5-enolpyruvylshikimate 3-phosphate synthase and result in reduced performance.

Increasing carrier water hardness from 0 to 1,000 mg L^{-1} reduced mesotrione efficacy by 28%, 18%, and 18% on giant ragweed, horseweed, and Palmer amaranth, respectively (Devkota et al. 2016a). Similarly, Devkota and Johnson (2016b) reported a linear trend in reducing 2,4-D choline and 2,4-D choline plus glyphosate efficacy on giant ragweed, horseweed, and Palmer amaranth control when carrier water hardness (resulting from $CaCl_2$ and $MgSO_4$) increased from 0 to 1,000 mg L^{-1}. According to Devkota and Johnson (2016b), increases in water hardness from 0 to 1,000 mg L^{-1} reduced weed control by 20% or greater with 2,4-D choline and premixed 2,4-D choline plus glyphosate. Schortgen and Patton (2021) also reported that water-soluble amine and choline formulations of 2,4-D were antagonized by hard water at 600 mg $CaCO_3$ L^{-1}. In a similar study, common lambsquarters, horseweed, redroot pigweed (Amaranthus retroflexus L.), and common ragweed control with 2,4-D was reduced with the presence of Ca^{2+} and Mg^{2+} in the spray water (Izadi Darbandi et al. 2011; Roskamp et al. 2013b). The result was attributed to the cations binding to the negatively charged herbicide ions, reducing the absorption into plants and rendering them less effective (Roskamp et al. 2013b).

Hard-water antagonism of weak-acid herbicides has been associated with variable response on weed species. Foxtail millet (Setaria italic L.) and yellow foxtail (Setaria pumila L) control by terbuthylazine plus mesotrione was reduced by hard-water antagonism; however, there was no response for common lambsquarters, common ragweed, and velvetleaf control (David and Mate 2010). Common lambsquarters control with 2,4-D was reduced by hard-water antagonism, whereas a similar response was not observed for horseweed (Erigeron canadensis L.) control (Roskamp et al. 2013a). The efficacy of glufosinate on velvetleaf, foxtail millet (Setaria italic L.), and red amaranth (Amaranthus cruentus L.) was reduced by hard-water antagonism (Zollinger et al. 2010, 2011). In contrast, the effect of water hardness was not observed on glufosinate for green foxtail, common lambsquarters, redroot pigweed, barnyard grass, and velvetleaf (Soltani et al. 2011). Roskamp et al. (2013b) observed hard-water antagonism on 2,4-D efficacy on control of common lambsquarters, but a similar response did not occur for saflufenacil efficacy. The variable response of weed species may be due to the differences in morphology and rate of herbicide absorption and translocation as affected by hard-water antagonism. For instance, Zollinger et al. (2010) observed greater absorption of ^{14}C-glufosinate by velvetleaf and giant foxtail than by common lambsquarters in the presence of Ca^{2+} and Mg^{2+} in the spray solution.

Spray Water Temperature and Herbicide Performance

Spray water temperature is influenced by ambient air if stored in an outside holding tank prior to herbicide application. The temperature of groundwater in the United States can vary from 3 C in northern states such as Indiana, Kansas, and Minnesota to 22 C in southern states such as Alabama, Florida, and Georgia depending on the application timing of the year (USEPA

2016). Moreover, when herbicide solution is stored in a spray tank, the herbicide spray water tends to be at equilibrium with the prevailing ambient air temperature (Ellis and Griffin 2002). The few available studies on this have shown that spray water temperature can adversely affect herbicide performance (Beltran et al. 2000; Devkota 2016; Singh et al. 2010). Spray water temperature can influence herbicide performance by affecting the rate of hydrolysis, degradation, physiochemical properties of spray mixture, and droplet size distribution (Beltran et al. 2000; Miller et al. 2005). Higher spray water temperature may lead to rapid conversion of herbicide active ingredient to an inactive compound, thereby reducing its efficacy (Beltran et al. 2000). For example, the degradation rate of isoxaflutole was faster at 50 C than at 22 C, although the inactive degradation product was not detected (Beltran et al. 2000). However, Rouchaud et al. (1998) reported that the degradation of isoxaflutole in spray water led to a rapid conversion into 2-methanesulfonyl-4-trifluoromethylbenzoic acid, an inactive benzoic acid derivative, resulting in reduced herbicidal activity on the target plants. Similarly, the half-life of chlorsulfuron was reduced from 5.59 d at a solution temperature of 20 C to 0.08 d at 55 C, indicating rapid dissipation and a possible efficacy reduction at a higher solution temperature (Grey and McCoullough 2012). Higher spray water temperature is also found to reduce surface tension, viscosity, and spray droplet size, resulting in increased vapor drift, reduction in spray interception by targeted plants, and sub-optimum droplet coverage (Miller et al. 2005; Miller and Tuck 2005). Miller et al. (2005) demonstrated that conventional nozzles resulted in smaller droplets size as spray water temperature increased up to 25 C. Similarly, Hoffmann et al. (2011) reported a reduction in surface tension, viscosity, and spray droplet size with increasing spray water temperature from 10 to 40 C.

Spray water temperature can also influence the solubility of the herbicide in water. Herbicides can become less soluble and form a precipitate at the bottom of the spray tank at a lower water temperature, which can result in poor target delivery of the active ingredient (Singh et al. 2010). For example, the water solubility of simazine decreased from 84 mg L^{-1} at 85 C to 6.2 mg L^{-1} at 22 C and 2 mg L^{-1} at 0 C (Wauchope et al. 1992). Similarly, acetyl co-enzyme A carboxylase (ACCase) inhibitors such as cyhalofop, fenoxaprop-p, metamifop, and quizalofop-p were reported to be less water soluble (<1 mg L^{-1}) at temperatures below 25 C (Table 1), indicating a potential for reduced efficacy at lower water temperature (Wauchope et al. 1992). The efficacy of clodinafop formulations on littleseed canarygrass (*Phalaris minor* L.) was decreased at 8 C compared with 25 C or 40 C, owing to the reduced solubility and subsequent target delivery of the herbicide at lower spray water temperature (Singh et al. 2010). The efficacy of diquat and endothall on curlyleaf pondweed (*Potamogeton crispus* L.) was inhibited as the water temperature in the tank decreased from 25 C to 10 C (Netherland et al. 2000). Similarly, glufosinate, mesotrione, 2,4-D choline, and premixed dicamba plus glyphosate efficacy on giant ragweed (*Ambrosia artemisiifolia* L.), pitted morningglory (*Ipomoea lacunosa* L.), Palmer amaranth, and horseweed (*Conyza canadensis* L.) was reduced at relatively low (5 C) or high (56 C) temperature, but the efficacy was not affected at spray water temperature between 18 C and 44 C (Devkota 2016; Devkota et al. 2016b). Those authors have also suggested that the herbicide efficacy could be affected at lower or higher spray water temperature due to the formulation instability, which subsequently inhibits uptake and weed control.

Spray Water Turbidity and Herbicide Performance

Inorganic (sand, silt, and clay) and organic matter, and sediments suspended in spray water can bind to herbicide molecules and reduce their performance (Frater et al. 2017). Spray water turbidity has been associated with reduced efficacy of paraquat (Simarmata et al. 2017); diquat (Fox and Murphy 1990; Hofstra et al. 2001; Poovey and Skogerboe 2003, 2004; Rytwo and Tavasi, 2003); endothall (Poovey and Skogerboe 2004); glyphosate (Simarmata et al. 2017); foramsulfuron (Nosratti et al. 2016); nicosulfuron (Hajmohammadnia-Ghalibaf et al. 2015, 2016; Nosratti et al. 2016); clethodim and sethoxydim (Gauvrit and Lamrani 2008; Singh et al. 2010); and imazosulfuron, diflufenican, and iodosulfuron (Shahbazi et al. 2015). Hajmohammadnia-Ghalibaf et al. (2015) reported reduced glyphosate and nicosulfuron efficacy on barnyardgrass and velvetleaf with the presence of soil particles in the spray water. Fox and Murphy (1990) observed reduced diquat efficacy on submerged weeds with water turbidity. Diquat activity on common waterweed (*Egeria densa* Planeh) and coontail (*Ceratophyllum demersum* L.) was reduced with the presence of bentonite clay sediment in the spray water (Hofstra et al. 2001; Poovey and Getsinger 2002). Herbicides such as paraquat and glyphosate with low soil mobility or with high soil adsorption coefficient (K_{oc}) can bind tightly to the suspended particles in the solution. The negative effect of spray water turbidity on herbicide efficacy has been attributed to the binding of sediment or negatively charged clay particles to the highly polar and positive-charged herbicide molecule, which resulted in a reduction in plant uptake (Poovey and Getsinger 2002). Cationic herbicides such as paraquat and diquat can adsorb strongly to negatively charged suspended particles (Bowmer 1982; Hofstra et al. 2001; Weber et al. 1965). Diquat efficacy was also reduced because of adsorption to montmorillonite and kaolinite clay particles in the spray solution (Bowmer 1982; Weber et al. 1965). Additionally, suspended particles in the spray solution can block sprayer nozzles/screens, thereby reducing the delivery of the herbicide to the target species, and also damage spray equipment (e.g., pumps; Aliverdi and Ahmadvand 2020; Poovey and Getsinger 2002).

Spray Mixture Storage Duration and Herbicide Performance

Unforeseen circumstances, such as unfavorable weather conditions, may prevent herbicide application immediately after mixing, thus prolonging the storage of a spray solution (Eure et al. 2013). The literature suggests that the time between herbicide spray mixture preparation and application can influence herbicide performance, especially for plant growth regulator herbicides such as dicamba and 2,4-D. The longer the herbicide remains in the solution, the greater the possibility for the herbicide molecule to break down or interact with constituents in the spray mixture (Lin et al. 2003; Stewart et al. 2009). Prolonged storage of an herbicide mixture in the spray tank can enhance herbicide binding to the interior surface of a polyethylene tank, herbicide settling out of solution, and subsequent efficacy reduction on targeted plants (Boerboom 2004; Lin et al. 2002). Chemical degradation can result from the interaction of the herbicide with the chemical components of water, or if in a tank-mix, with other herbicides in the mixture (Lin et al. 2002; Stewart et al. 2009; Thelen et al. 1995). Stewart et al. (2009) observed that velvetleaf and common lambsquarters control was reduced by 37% and 17%, respectively, when isoxaflutole plus atrazine was stored for 7 d. Isoxaflutole efficacy reduction was attributed to the conversion of the degradative product of the herbicide (diketonitrile) into the inactive benzoic acid product

(Pallett et al. 2001; Stewart et al. 2009). Isoxaflutole is a pro-herbicide and does not have herbicidal activity unless it is converted to the degradative product diketonitrile in targeted plants (Pallett et al. 1998). However, if the degradation occurs in the spray solution because of longer storage duration, then diketonitrile can interact with hypochlorite salt in water and form the nonbiologically active benzoic acid derivative (Lin et al. 2003; Stewart et al. 2009). Lin et al. (2003) further reported that diketonitrile reacted with hypochlorite salt in water and was degraded completely to an inactive benzoic acid compound in less than a minute.

Dimethenamid-P plus dicamba plus atrazine, and rimsulfuron plus *S*-metolachlor plus dicamba efficacy on velvetleaf was reduced by 50% when the spray mixture was in the tank for 3 to 7 d after mixing (Stewart et al. 2009), compared to application immediately after mixing. It is possible that the prolonged storage of the aforementioned herbicides mixture could have led to the adherence of dicamba to the inside surface of the spray tank. Synthetic auxin herbicides such as dicamba and 2,4-D have the potential to adhere to the spray tank (Boerboom 2004).

The impact of spray mixture storage duration on herbicide efficacy is often found to be inconsistent depending on herbicides and targeted weed species (Boerboom 2004; Eure et al. 2013). Isoxaflutole and dicamba efficacy on velvetleaf and common lambsquarters was reduced when spray application was delayed for 3 to 7 d after mixing. In contrast, the efficacy of glyphosate, glufosinate, mesotrione plus atrazine, premix dicamba plus diflufenzopyr, and premix nicosulfuron plus rimsulfuron was not affected (Stewart et al. 2009). Similarly, spray mixture storage duration up to 9 d after mixing did not negatively affect pendimethalin, *S*-metolachlor, fomesafen, flumioxazin, diclosulam, imazethapyr, and dimethenamid-P for common lambsquarters, Palmer amaranth, and broadleaf signalgrass control (Eure et al. 2013). Devkota et al. (2016b) demonstrated that the efficacy of premixed glyphosate plus dicamba on horseweed, pitted morningglory, giant ragweed, and Palmer amaranth was not affected with storage of spray solution for 6 to 24 h prior to application. Overall, the variation in weed control response of herbicides in relation to the spray solution storage duration has been attributed to binding to the spray tank and the formation of degradative products or intermediate compounds. Additionally, the response can vary with weed morphology; for example, velvetleaf (with the presence of dense hairs on the leaf) can inhibit the absorption of diketonitrile compared to other species without hairs (Pallett et al. 2001).

Adjuvants for Amending Spray Water Quality and Improving Herbicide Performance

Adjuvants are additives used for amending spray solution and improving herbicide performance (Pratt et al. 2003). Spray adjuvants consist of oils, wetting agents, and surfactants formulated to improve emulsification, dispersion, absorption, and penetration of herbicides on targeted plants. Adjuvants also consist of spray buffers to adjust solution pH, water conditioners to amend hard water, drift retardants to reduce herbicide drift, and suspension aids to enhance the mixing of the herbicide formulation (Culpepper et al. 1999; Thelen et al. 1995). Adjuvants can improve herbicide performance by enhancing retention and absorption by plants. However, improved herbicide performance by adjuvants depends on herbicide solubility, type of cations present, pH of the spray solution, and the adjuvant surfactant characteristics such as concentration, ethoxylation, and lipophilic-hydrophilic balance (Devkota and Johnson 2019; Green et al. 1996).

Ammonium sulfate (AMS) and dipotassium phosphate are water conditioning adjuvants commonly used to overcome hard-water antagonism and improve herbicide efficacy against hardness cations (Bernards et al. 2005; Devkota and Johnson 2016b; Nalewaja and Matysiak 1993). Glyphosate efficacy was improved with the use of AMS, and this was attributed to the increase in absorption (Bernards et al. 2005). Furthermore, AMS prevented the interaction of manganese and glyphosate in the spray solution, thereby improving the control of velvetleaf and giant foxtail by glyphosate. The addition of AMS also improved mesotrione, glufosinate, dicamba, and 2,4-D choline efficacy on common lambsquarters, redroot pigweed, giant ragweed, horseweed, and Palmer amaranth by overcoming the antagonistic effect of Ca, Mg, and Mn cations (Devkota 2016; Roskamp et al. 2013a, 2013b). Similarly, the efficacy of glyphosate on pitted morningglory, entireleaf morningglory (*Ipomoea hederacea* var.), palmleaf morningglory (*Ipomoea wrightii* var.), johnsongrass (*Sorghum halepense* L.), velvetleaf, prickly sida (*Sida spinosa* L.), hemp sesbania (*Sesbania exaltata* L.), common lambsquarters, giant foxtail, and sicklepod (*Senna obtusifolia* L.) was increased with the addition of AMS (Jordan et al. 1997; Roggenbuck and Penner 1997; Salisbury et al. 1991; Satichivi et al. 2000). The increased herbicide performance with AMS was attributed to longer retention of spray droplet on the leaf surface and improved penetration through the leaf cuticle and cell membrane (Pratt et al. 2003; Thelen et al. 1995). Nalewaja and Matysiak (1993) also suggested that the effect of AMS against hard-water cations is due to the potential of the sulfate (SO_4^{2-}) anions of AMS to bind with cations such as Mg^{2+}, Ca^{2+}, Na^+, and K^+ and prevent the herbicide-cation complex formation. Thelen et al. (1995) reported that the direct interaction between glyphosate molecule and NH_4^+ cation for NH_4^- glyphosate formation, could be the possible mechanism for AMS enhancing herbicide efficacy. It is further speculated that NH_4^- glyphosate may be more readily absorbed than glyphosate-calcium salt complex, thereby increasing weed control efficacy. Whitford et al. (2014) also suggested that adjuvants such as AMS can minimize spray droplet evaporation (i.e., droplets remain on the leaf surface longer), which can facilitate herbicide uptake into the leaf.

Variable responses to the addition of AMS have been reported for some herbicides and weed species. AMS overcame calcium antagonism of glyphosate efficacy on wild oat (*Avena fatua* L.), littleseed canarygrass, and redroot pigweed, but a similar result was not observed on kochia [*Bassia scoparia* (L.); Mirzaei et al. 2019]. Additionally, Mirzaei et al. (2019) observed a higher effectiveness of AMS on redroot pigweed than on wild oat and littleseed canarygrass. Glyphosate efficacy was enhanced with the addition of AMS for perennial horsenettle (*Solanum carolinense* L.) control; however, a similar effect was not observed for common lambsquarters, sicklepod, and giant foxtail control (Pline et al. 2000). Glufosinate efficacy on barnyardgrass, giant foxtail, and velvetleaf was enhanced by AMS, but redroot pigweed and common lambsquarters control was not affected (Maschhoff et al. 2000). The inconsistent weed species responses to herbicide applied with AMS may be due to the variation in the crystalline nature of epicuticular wax, and relative amount of nonpolar and polar waxes on the leaf cuticle (Harr et al. 1991). For instance, the ratio of polar to nonpolar waxes has been reported at 1.5 and 12.1 for purple nutsedge and sicklepod, respectively (Green and Hale 2005). Similarly, the epicuticular wax content in most weed species varies between 10 to 200 µg cm^{-2} (McWhorter 1993). Such large differences in polar to nonpolar wax ratio and variation in epicuticular wax content among the weed species can affect the herbicide penetration

through the cuticle resulting in reduced herbicide activity (Green and Hale 2009; Liu and Gaskin 2004; Liu et al. 2004).

Other ammonium-containing fertilizers such as ammonium phosphate, urea ammonium nitrate, and ammonium polyphosphate are also commonly used to overcome mineral-cation antagonism and improve herbicide performance (Nalewaja and Matysiak 1993; Nalewaja et al. 1991). Ammonium fertilizer can decrease surface tension, prevent the formation of precipitates, and increase herbicide penetration through the leaf (Nalewaja et al. 2000; Tu and Randall 2003). Ammonium fertilizers increased glyphosate efficacy on quackgrass (Blair 1975; Turner and Loader 1981) and barley [*Hordeum vulgare;* O'Sullivan et al. 1980]. Similarly, ammonium-containing fertilizer additives increased sethoxydim efficacy on johnsongrass, quackgrass (*Agropyron repens* L.), *Setaria* spp., and shattercane [*Sorghum bicolor* L.; McKeague et al. 1986]. Koger et al. (2007) also reported that addition of urea ammonium nitrate (UAN) shortened the rain-free period from 8 to 1 h and improved barnyardgrass control with bispyribac.

Buffering agents are also used to modify or maintain spray solution pH and increase the solubility of herbicides in acidic or alkaline spray water. Striegel et al. (2021) observed that the addition of MON 51817, a pH buffer to a diglycolamine salt of dicamba, increased the spray solution pH from 4.96 to 5.34. Similarly, Mueller and Steckel (2019) reported that pH buffers such as Norvus K (Innvictis Crop Care, Loveland, CO), ChemPro CP-70 (Chemorse, Des Moines, IA), and SoyScience (AgXplore, Parma, MO) increased the pH of glyphosate plus N, N-Bis-(3-aminopropyl) methylamine salt and diglycolamine salt of dicamba mixtures from 4.6 to greater than 5.0.

Conclusions and Implications for Future Research

Summary
Spray water quality has profound implications on herbicide spray solution and weed control efficacy. The available literature suggests that the weed control potential of herbicides can be antagonized by spray water quality. Among the spray water quality factors, pH is the most important, followed by hardness, temperature, turbidity, and storage duration. These factors can alter the properties of a herbicide active ingredient during mixing, while the spray mixture remains in the tank, during the application processes, and after deposition on the target. These effects can be observed as tank-mixing incompatibility, reduced solubility, rapid hydrolysis and degradation, formation of herbicide-mineral complex, binding of herbicide molecule with suspended particles, change in droplet size and evaporation rate, and crystalline salt deposits on the leaf surface. Furthermore, effects can be pronounced on total absorption and translocation, which reduces overall performance depending upon herbicide chemistry and weed species. The leaf morphology can also play an important role in influencing herbicide efficacy regarding the spray water quality. Leaf structures such as trichomes, nature of epicuticular wax, and cuticle thickness are some of the characteristics that can confound with spray water quality factors and influence herbicide efficacy.

The key findings suggest that the efficacy of sulfonylureas is negatively affected by acidic water pH, whereas the efficacy of weak-acid herbicides such as glyphosate, glufosinate, clethodim, sethoxydim, bentazon, and 2,4-D is improved under this condition. The efficacy of HPPD-inhibitor herbicides can be improved with acidic or alkaline spray water pH depending on the weed species. Control of weed species such as barnyardgrass, broadleaf signalgrass, common cocklebur, giant ragweed, horseweed, large

crabgrass, palisade grass, Palmer amaranth, and Texasweed can be reduced by non-optimal spray water pH. Hard-water antagonism is more prevalent with weak-acid herbicides, with trivalent cations such as Fe^{3++} being the most problematic. Control of weed species such as common lambsquarters, giant foxtail, giant ragweed, horseweed, Palmer amaranth, velvetleaf, and yellow nutsedge are primarily affected by hard-water antagonism to various degrees depending on the herbicides and cations. AMS and other ammonium-containing fertilizers can help to overcome the hard-water antagonism of weak-acid herbicides; however, the response varies with the herbicide and targeted weed species. Spray solution temperature between 18 C and 44 C is the optimum for most weak-acid herbicides, whereas efficacy is reduced at relatively low (5 C) or high (56 C) temperatures. Cationic herbicides such as paraquat and diquat, and herbicides with low soil mobility such as glyphosate, are most susceptible to the antagonistic effect of spray water turbidity; therefore, clean water should be used to mitigate water turbidity issue. The reduction in efficacy with respect to spray mixture storage duration is primarily due to herbicide adherence to the spray tank (dicamba), and herbicide degradation to a nonactive compound (isoxaflutole).

Future Research
A significant number of published research findings on spray water quality suggest that herbicide properties are influenced by spray water quality factors before, during, and after application. However, most of these studies have focused on single water-quality factors with greenhouse experiments conducted on individual weed species, which may not truly predict herbicide and weed responses under field conditions. Moreover, information on the effect of spray water quality factors is not available for many of the herbicides currently used to manage glyphosate-resistant weeds. This warrants extensive research on the potential effects of spray water-quality factors on different herbicide chemistries and formulations across diverse weed categories. It is particularly necessary to conduct field research to evaluate multiple water-quality factors and their interactions on herbicide efficacy with a focus on problematic weed species. Most of the published research on the effect of adjuvants in adjusting water quality are primarily focused on using AMS for addressing spray water hardness. There is no published research evaluating spray buffers for amending solution pH and optimizing herbicide efficacy against spray water pH. Additionally, research needs to be conducted focusing on adjuvants for addressing spray water hardness and pH for improving herbicide efficacy. Research findings generated from such studies will be important in developing guidelines for optimizing herbicide efficacy for effective weed control.

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