

Review

Glyphosate Efficacy of Different Salt Formulations and Adjuvant Additives on Various Weeds

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Abstract: In many crops, weeds are managed by herbicides, mainly due to the decrease in crop yields and farmers' incomes caused by them. In general, chemical control of weeds is considered to be an easy, relatively cheap, and highly effective method. However, not all weeds can be successfully controlled, either because of their natural tolerance or their herbicide resistance. Glyphosate is one of the most widely used herbicides in the world. It can manage effectively a broad spectrum of weeds, and promotes conservation agriculture by significantly reducing conventional plough tillage. Unfortunately, its extensive use has led to the evolution of glyphosate resistance, which has evolved into a major problem for global crop production. Alternative herbicides are, in some cases, available, but they do not usually control certain weeds as efficiently as glyphosate. The transmission of herbicides to the target site is a complex process, and consists of several stages. Each herbicide is affected and can be manipulated by the product formulation for the optimization of its use. Many experiments have confirmed that different glyphosate salts and adjuvant additives are instrumental in the optimization of herbicide absorption and delivery processes. The objective of this paper is to provide a brief overview of these experiments and summarize the literature related to the effect of various glyphosate formulations and adjuvants on weed control. Determining the differences among formulations and adjuvants may lead to the further optimized long-term use of glyphosate.

Keywords: glyphosate; resistance; salts; adjuvants; weeds

1. Introduction

Herbicides have been recognized as one of the most efficient tools against weeds since their widespread adoption in the decade following 1940, while nowadays they clearly account for over 1/3 of the total pesticide volume consumed [1]. To be effective, herbicides should adequately contact, be absorbed by and move within plants without losing their toxic effect till the site of action [2]. Differences in weed biology have led to many types of herbicides with different modes of action and product formulations. Variability of herbicides aims at a greater diversity and efficacy in herbicide use. In addition, herbicide efficacy can be significantly influenced by environmental conditions, adjuvants and spray carrier water quality [3–8]. In particular, glyphosate efficacy is influenced by air temperature and light intensity [9,10]. Moreover, the pH of the tank mix can increase herbicide solubility and efficacy [11]. As a result, the optimum herbicide performance is significantly affected by the interaction of all of the above factors.

Glyphosate [*N*-(phosphonomethyl) glycine] is a non-selective, systemic, post-emergence herbicide that economically controls many weeds in a wide range of both agricultural and non-agricultural situations [12]. This active ingredient is responsible for several metabolic disturbances, as it inhibits aromatic amino acid biosynthesis by blocking the shikimic acid pathway at the growing parts of

plants [13,14]. Moreover, it is widely considered to be the most important herbicide in global agriculture due to its many desirable characteristics and its wide use in genetically modified (GM) crops [12,15].

Over the last few years, continuous usage of the same herbicides has resulted in the decrease of their efficacy against an increasing number of weed species [16,17]. In particular, 479 unique cases (species \times site of action) of herbicide-resistant weeds, with 251 species, have been recorded globally by the International Survey of Herbicide-Resistant Weeds [18]. In the case of glyphosate, no evolved resistance was reported until 1996, when glyphosate-resistant rigid ryegrass was recorded for the first time [19]. Since then, the number of glyphosate-resistant (GR) weeds has progressively increased. Despite the existence of alternative herbicides, such as diquat and glufosinate, glyphosate still remains the most effective herbicide for controlling very small or large perennial weeds [17,20,21]. Consequently, the evaluation of the various available glyphosate formulations with view towards the optimization of its performance is imperative.

Herbicide molecules that are weak acids, such as the glyphosate parent acid, may be altered in order to enhance the handling and stability of the herbicide formulation. In this case, the acidic carboxyl hydrogen is either replaced by the desired ions from a salt or it is placed to react with an alcohol to form an ester [22]. Today, there are many available commercial formulations of glyphosate in the forms of isopropylamine, diammonium, monoammonium, potassium, trimethylsulfonium and sesquisodium salts.

Commercial glyphosate formulations usually contain a monovalent salt of glyphosate, due to their high water solubility [23,24]. Glyphosate salts perform a variety of important functions. In particular, the salt portion of the formulated product may allow for greater absorption of glyphosate through its more effective penetration into the leaf [22]. However, the salts do not have an impact on the herbicidal activity, since only the parent acid acts at the target site within the plant. When comparing different salt formulations with the same active ingredient, the acid equivalent of the formulation should be taken into consideration [22]. Consequently, differences in the theoretical yield of the parent acid of formulated products applied could be observed under these circumstances.

In addition, various types and amounts of adjuvant additives, either included in the formulated products or added in the tank mixture, have been found to improve glyphosate performance in different ways. For instance, surfactants, the most commonly used adjuvants, can activate herbicide diffusion across the cuticle by penetrating into the plant cuticle and improving herbicide uptake [25]. It is also worth mentioning that formulations may differ with respect to the quantity of glyphosate that can ultimately be concentrated, due to the different molecular weights of different salts, and the various adjuvants that have been used by different manufacturers [26].

In relation to herbicide targeting efficiency, adjuvants may be used to modify spray droplet formation, droplet impaction and spray retention of the leaf surface, spreading, coverage and deposit formation [27]. Surfactants play an important role in the retention and absorption of glyphosate by the plant surface. In particular, they offer a unique balance of lipophilic and hydrophilic properties, and can serve as a solvent for herbicides on the leaf surface [25]. Moreover, some surfactants seem to enhance the solubility of the herbicide in the wax [28,29] and induce direct stomatal infiltration of the spray solution [30,31]. Finally, surfactants are able to allow more intimate contact between herbicide and plant surface by reducing the surface tension of spray solution [32].

Ammonium fertilizers constitute another important type of adjuvants. Among the others, ammonium fertilizers can prevent the formation of particulates in the tank mix, decrease surface tension, increase herbicide spreading and penetration into the leaf [33,34]. Furthermore, ammonium has proved to be more effective than sodium salts as adjuvants in glyphosate, with ammonium sulfate being the most effective among the several sulfate compounds [35]. This is probably due to the fact that the NH_4^+ ion is not competitive with glyphosate and may enhance glyphosate efficacy. It has also been reported that ammonium sulfate can significantly improve herbicide activity when weeds are grown under water-stress conditions [36].

The purpose of this paper is to present some of the different glyphosate formulations and adjuvants, along with their impact on the efficacy of the herbicide. Inevitably, the space constraints of this condensed review and the ongoing research on the topic make detailed presentation of all the relative studies carried out by all the authors mentioned herein impossible. Despite these limitations, this paper aims to emphasize the basic differences among some of the various glyphosate products and encourage further research based on the diverse references.

2. Effect of Salt Formulation on Glyphosate Efficacy

In many cases, the differences in absorption and translocation of the herbicide are responsible for the fluctuation in glyphosate efficacy and the variations in glyphosate tolerance among weed species [37]. Such differences between isopropylamine and diammonium salt formulations were recently reported by Li et al. [38]. In particular, three commercial formulations of glyphosate, i.e., the isopropylamine salt formulated as Roundup Ultra (IPA1) and Roundup UltraMax (IPA2) and the diammonium salt formulated as Touchdown IQ (DA) were applied at a rate of 750 g a.eha⁻¹, in three- to five-leaf velvetleaf (*Abutilon theophrasti* Medik.), common waterhemp (*Amaranthus rudis* L.), and pitted morning glory (*Ipomoea lacunose* L.). Concerning common waterhemp, initial absorption of glyphosate was higher with the isopropylamine formulations compared to the diammonium formulation by 2 h after treatment (HAT). In pitted morning glory, higher foliar absorption was observed in plants treated with the DA than in plants treated with the IPA formulation 6 HAT. In addition, glyphosate translocation to the roots was 27% higher in the case of the DA salt formulation compared to the IPA formulation at 74 HAT. However, the initial slight differences in absorption and translocation in the weed species did not affect the overall efficacy of the three glyphosate formulations at 74 HAT. A previous study by Satchivi et al. showed no significant difference in the absorption and translocation of the isopropylamine (Roundup Ultra) and trimethylsulfonium (Touchdown) glyphosate salts in velvetleaf and giant foxtail (*Setaria faberi* Herm.) [36]. The authors attributed this absence of differences to the equal active acid glyphosate yield in the two formulations. On the contrary, velvetleaf absorbed more glyphosate formulated as isopropylamine salt compared to the trimethylsulfonium formulation according to Feng et al. [39].

Another study compared the efficacy of three different glyphosate formulations, i.e., isopropylamine salt (Roundup Ultra), trimesium salt (Touchdown) and glyphosate acid with 1-aminomethanamide dihydrogentetraoxosulfate (Engame) in relation to the control of prickly sida (*Sida spinosa* L.), entire leaf morning glory (*Ipomoea hederacea* var. *integriuscula* Gray), sicklepod (*Senna obtusifolia* (L.) H.S. Irwin & Barneby) and purple nutsedge (*Cyperus rotundus* L.) [40]. In all tested weeds, the GR₅₀ values for Engame were 2–3-fold lower than those determined for the isopropylamine and the trimesium salts, indicating that tetraoxosulfate was 2–3 times more active than the other formulations, on an acid equivalent basis. The responses of prickly sida, sicklepod and purple nutsedge to Roundup Ultra and Touchdown were similar. However, morning glory was more susceptible to the trimesium than to isopropylamine salt, as indicated by the dose-response curves. These results confirm that glyphosate efficacy can be further enhanced by formulations that apparently improve acid uptake [41].

The efficacy of a new potassium salt formulation of glyphosate against other formulations of glyphosate was evaluated by Golob et al. [42] in many broadleaf and grass weeds. The potassium salt formulation resulted in a better control of all weed species, compared to the isopropylamine salt formulation at 14, 28, and 56 days after treatment (DAT). However, it is important to note that different rates of mono potassium and isopropylamine salt formulations were applied, and this could be one of the reasons for such observations.

In the case of glyphosate droplets application, efficiency of weed control can increase if the herbicide formulation provides higher target coverage and evaporation time, by allowing the herbicide absorption to continue even after the droplets evaporation. In recent research, Oliveira et al. assessed the influence of glyphosate formulations on the wetted area and evaporation time of glyphosate

droplets on different surfaces target weeds [43]. Tests were conducted with droplets 500 µm in diameter, containing three formulations of glyphosate (isopropylamine salt, ammonium salt and potassium salt), which were deposited on three surfaces, two leaves (*Bidens pilosa* L. and *Cenchrus echinatus* L.) and one glass slide. It should be mentioned that the glyphosate formulations were of the same quantity of acid equivalent in all treatments. According to the results, the isopropylamine salt decreased the wetted area and evaporation time compared to ammonium salt and potassium salt for all three surfaces. In particular, the potassium and ammonium salt formulations showed higher wettability when applied to *B. pilosa* leaves, while the isopropylamine salt formulation resulted in lower wettability on *C. echinatus* leaves and the glass slide. The potassium salt formulation on the leaf surface of *C. echinatus* showed the highest evaporation time among all treatments, and isopropylamine salt formulation showed the lowest evaporation time for the droplets on all deposition surfaces. Some of these differences could be attributed to the different leaf anatomy and surface of broadleaf and grass weeds. The outcome of this research confirms that interaction among glyphosate formulations and leaf surfaces should be taken into consideration, as they may be crucial to the efficacy of the formulations. Similar differences can be crucial in the case of weeds with hair coverage like in *Conyza* spp. and therefore the selection of the most suitable salt could potentially be of some importance [17,20].

Two different formulations of glyphosate, isopropylamine (Accord SP) and ammonium (Roundup Pro Dry) salt of glyphosate were studied against Chinese privet (*Ligustrum sinense* Lour.) [44]. Results showed that control of cover, density and height of Chinese privet did not differ significantly between the two formulations. However, this study was conducted only under dry conditions (summer), and probably with a reduced herbicide uptake and translocation, and therefore the results cannot be generalized.

In a study by Richardson et al. [45], weed control was independent of glyphosate salt. In particular, control of common ragweed (*Ambrosia artemisiifolia* L.), ivyleaf morning glory (*Ipomoea hederacea* Jacq.), pitted morning glory and large crabgrass (*Digitaria sanguinalis* (L.) Scop.) at 25DAT was similar for both isopropylamine and diammonium salts of glyphosate, at selected rates ranged from 0.42 to 3.36 kg ae/ha.

3. Influence of Surfactants on Glyphosate Efficacy

The formulation of a herbicide, particularly the adjuvant systems, can significantly influence the efficiency of herbicide uptake and translocation within the plant [46]. Surfactants are active primarily on the leaf surface, and enhance glyphosate uptake, translocation and field performance. The effect of ethylene oxide (EO) chain length of three homologous series of nonionic surfactants on glyphosate uptake was studied by Knoche and Bukovac [47]. The results of their study revealed significant effects of leaf surface properties on surfactant enhancement of pesticide uptake. Glyphosate-monoammonium formulation containing Trimao (8PO) provided the highest uptake in white mustard (*Sinapis alba* L. cv. Alba), regardless the addition of ammonium sulfate [48].

To associate the surfactant mechanism of action with surfactant type, one of the most important measures assigned is the hydrophile/lipophile balance (HLB). Usually low HLB surfactants are more lipophilic and thus more able to diffuse into the lipophilic cuticle than high-HLB surfactants [25]. Nalewaja et al. [49] studied the influence of nonylphenoxy surfactants and glyphosate salt formulation on spray retention, phytotoxicity and glyphosate uptake in summer cypress (*Kochia scoparia* (L.) Schrad). Glyphosate spray retained by *K. scoparia* was higher with increasing hydrophilic-lipophilic balance (HLB) value of surfactants. Specifically, the spray contained nonylphenoxy surfactants with HLB values of 15.0 and 17.2. Spray retained by *K. scoparia* was higher for the surfactant with HLB of 17.2 than 15.0. These results indicate that the increase in glyphosate phytotoxicity in *K. scoparia* was partially due to the higher spray retention.

In another study, Sharma and Singh [50] evaluated the influence of non-ionic (X-77) and organosilicone (L-77) adjuvants and methylated seed oil (MSO) on the uptake, translocation and efficacy of glyphosate in *Bidens frondosa* L. and *Panicum maximum* Jacq. In *B. frondosa*, all three adjuvants

significantly increased the uptake and translocation of glyphosate. In the presence of L-77, more than 50% of the applied glyphosate was taken up by *B. frondosa* within 15 min. At 6 h, and thereafter, glyphosate uptake was significantly higher with MSO compared with X-77. In *P. maximum*, uptake and translocation of glyphosate increased with both X-77 and MSO, but not with L-77. In fact, an antagonistic effect on uptake and translocation of glyphosate and L-77 was revealed in this grass species. These differences should certainly be studied in more weed species before attributing them to the differences between broadleaf and grass weeds.

Similarly, in field experiments where glyphosate was applied alone or formulated with surfactants (non-ionic, organosilicone), the addition of the latter increased the control in lantana (*Lantana camara* L.) and Groundsel bush (*Baccharis halimifolia* L.). In particular, the increase of glyphosate efficacy was significantly higher in the non-ionic surfactant (Agral 90) compared to the organosilicone surfactant (Pulse) [51]. The same authors confirm that the application of glyphosate with various adjuvants, such as ammonium sulfate, x-77, Agri-dex, AN, Kinetic, urea, MSO to black nightshade (*Solanum nigrum* L.), wild mustard (*Sinapis arvensis* L.), large crabgrass and barnyard grass (*Echinochloa crus-galli* (L.) Beauv) significantly increased weed control compared to glyphosate alone [52]. Finally, Kirkwood et al. [53] also mentioned that the incorporation of the surfactant MON 0818 had enhanced herbicidal activity, absorption, translocation and sink accumulation of glyphosate.

4. Effect of Ammonium Sulfate (AMS) on Glyphosate Efficacy

Glyphosate is usually applied with ammonium sulfate (AMS) in order to reduce water hardness and enhance herbicide activity [54,55]. More specifically, common cations, such as sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^+), iron (Fe^{2+} or Fe^{3+}) and zinc (Zn^{2+}), bind strongly to glyphosate negatively charged molecules, and form salts that are not readily absorbed by plants [35,56]. The beneficial effect of ammonium sulfate on glyphosate efficacy has been reported in many studies [57–64]. For instance, control of johnsongrass (*Sorghum halepense* (L.) Pers.) with glyphosate [65] and absorption of glyphosate by *K. scoparia* were both increased with the addition of ammonium sulphate and regardless of the surfactant [49].

Sing et al. [52] showed that the application of glyphosate with various adjuvants, including ammonium sulfate, significantly increased weed control compared to glyphosate alone. However, the improvement in bioefficacy depends on both the type of the adjuvant and the weed species. An increase of herbicide efficacy on perennial horsenettle (*Solanum carolinense* L.) with the addition of ammonium sulfate to glyphosate was also reported by Pline et al. [66]. On the contrary, in the same study, giant foxtail, common lambsquarters (*Chenopodium album* L.) and sicklepod control by glyphosate was not influenced by the addition of ammonium sulphate.

AMS addition into water can also result in a higher absorption and translocation of the herbicide [67]. Satchivi et al. [36] found that glyphosate absorption by velvetleaf and giant foxtail was enhanced by the addition of 1% ammonium sulfate in either isopropylamine or trimethylsulfonium salt formulations. Quite interestingly, the addition of AMS in both glyphosate formulations increased the quantity of glyphosate translocated out of the treated leaf, but no difference was observed in the quantity of glyphosate translocated to the roots at any time. The report of Roggenbuck and Penner [68] in velvetleaf, common lambquarters and giant foxtail had shown same positive results for AMS in glyphosate activity. The improvement of glyphosate efficacy with the addition of AMS in trumpet creeper (*Campsis radicans* (L.) Seem. ex Bureau) was also reported by Chachalis et al. [69].

Similarly, application of 1% wt/v AMS in the spray mixture enhanced efficacy in six different formulations of glyphosate according to the study of Ramsdale et al. [70]. In the same study, it was shown that low spray volumes also maximized glyphosate efficacy, even in the presence of AMS, through high herbicide concentrations in the spray deposit and overcoming of the antagonistic salts. De Ruiter et al. [55] indicated that ammonium sulfate added to glyphosate-surfactant combinations reduced significantly ED_{50} values for glyphosate. Moreover, De Ruiter and Meinen [71] found that

the absorption of glyphosate by protoplasts, isolated from quackgrass (*Elytrigia repens* L.), was higher when ammonium sulphate was applied.

Weed control by glyphosate alone or with ammonium sulfate was evaluated by Jordan et al. [72] in velvetleaf, prickly sida, sicklepod, pitted morning glory, entireleaf morning glory, palmleaf morning glory (*Ipomoea wrightii* Gray) and hemp sesbania (*Sesbania herbacea* (Mill.) McVaugh). The results have shown enhancement of prickly sida and entireleaf morning glory control by ammonium sulfate. Particularly, entireleaf morning glory control increased from 44 to 50% when ammonium sulfate was added. Similarly, prickly sida control increased by 8 to 30% in three different experiments with the addition of AMS.

5. Conclusions

Numerous studies have been conducted to evaluate some of the factors that may result in differentiation of glyphosate efficacy. Many of them are presented in the current review. Concerning salt formulation of glyphosate products, the responses of various weed species vary among the different formulations. For instance, absence of significant differences was demonstrated for prickly sida, sicklepod and purple nutsedge to isopropylamine and trimesium salt formulations, whereas morning glory was more susceptible to the trimesium than to isopropylamine salt. In parallel, conflicting results occurred for a specific weed, i.e., velvetleaf, treated with different glyphosate salts.

The influence of adjuvants is also species-dependent and significant differences were reported among the numerous available surfactants. Organosilicone adjuvants antagonized glyphosate activity in the case of *Panicum maximum*. Interaction between leaf surfaces of weeds and different glyphosate salts or surfactants should also be taken into consideration.

Finally, ammonium sulfate constitutes another key factor to glyphosate efficacy. In the majority of studies its beneficial effect on the improvement of weed control has been confirmed. However, differences were observed among glyphosate formulations and weed species. For instance, the perennial horsenettle control was positively affected, whereas giant foxtail, common lambsquarters and sicklepod controls were not affected by the addition of AMS.

Nevertheless, the interactions between glyphosate salt formulations and adjuvants, on the one hand, and glyphosate performance on the other hand are complex, case-specific and depend on many factors, including plant characteristics of the target species, environmental conditions, adjuvant type and chemical form of the herbicide. Further research is essential to understanding the different roles of adjuvants in enhancing glyphosate efficacy for optimum utilization of this important herbicide.

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