Herbicides and Adjuvants

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Abstract

Adjuvants are any substance either added in a herbicide formulation or added to the spray tank that modifies herbicidal activity or application characteristics, such as better mixing and handling, increasing droplet coverage, spray retention and droplet drying, increasing herbicide cuticle penetration and cellular accumulation reducing leaching of herbicide through the soil profile, etc. The interactions between herbicide adjuvants and herbicide activity, however, are not simple processes, and depend on factors that include crop/weed leaf surface, droplet characteristics, adjuvant type, chemical form of the herbicide, and environmental conditions. Understanding the complexity of these interactions is essential for optimum herbicide utilization, particularly in prolonging, enhancing and improving the efficacy; reduction of the critical rain-free period; minimizing herbicide leaching into groundwater; and decreasing harmful effects to non-target plants and animals.

Keywords: Herbicide adjuvants, history, classification, interaction

1. Introduction

Adjuvants (from Latin, *adiuvare:* to aid) are commonly used in agriculture to improve the performance of herbicides or other pesticides, including better mixing and handling, increased effectiveness and safety, better distribution, and drift reduction [1]. There are many definitions for adjuvants. According to the American Society for Testing Materials (ASTM) [2] "adjuvant is a material added to a tank mix to aid or modify the action of an agrichemical, or the physical characteristics of the mixture." Broadly defined, "an adjuvant is an ingredient that aids or modifies the action of the principal active ingredient" [3] or a "formulant designed to enhance the activity or other properties of a pesticide mixture" [4]. Ferrell *et al*. [5] briefly describe adjuvants as "substances used with a pesticide to enhance its performance." Many other authors defined adjuvants, particularly herbicide adjuvants, in more detail. According to the Weed Science Society of America (WSSA) [6] "an herbicide adjuvant is any substance in a herbicide formulation or added to the spray tank to improve herbicidal activity or application characteristics" or "an adjuvant is any compound that can be added to a herbicide formulation to facilitate the mixing, application, or effectiveness of that herbicide" [7,8]. For Storrie *et al*. [9] adjuvants are "any substance either in an herbicide formulation or added to the spray tank, that modifies herbicidal activity or application characteristics." According to the last definition, adjuvants are already included in the formulations of some herbicides available for sale, or they may be purchased separately and added into a tank mix prior to use [10].

In order to be effective, herbicides must overcome a variety of barriers (morphological, biological, and environmental) to their entry into plants. For example, trichomes on the leaf surface can reduce herbicide efficacy by intercepting spray droplets before they contact the epidermal surface [11]. Environmental stress (e.g., hot, dry weather) may develop a thicker than normal wax layer, or increase other defensive structures such as reducing the plant's metabolic and transport processes that are required for adequate weed control.

Because of these reasons, adjuvants have been developed to assist herbicides, in that they:

- Allow better mixing and handling with herbicide active ingredient [12]
- Reduce or even eliminate spray application problems [13] (e.g., drift reduction) [14,15]
- Allow contact to the weed target, increase droplet coverage, spray retention, and droplet drying [16,17]
- Increase herbicide cuticle penetration and cellular accumulation [18,19]
- Significantly enhance and improve an herbicide's efficacy so that the concentration or total amount of herbicide required to achieve a given effect is reduced [20-26]
- Decrease the amount of herbicide applied and lower total costs for weed control [27,28]
- Enhance the formulation's ability to kill the targeted species without harming other plants [29]
- From an environmental aspect, can reduce leaching of herbicide through the soil profile [30,31]

However, it is important to note that in some circumstances, adding adjuvants will not significantly improve control [32]. Sometimes adjuvants can have negative effects, such as:

- Decreasing the activity of the herbicide (antagonistic effects) [33]
- Increasing the formulation's ability to spread or persist in the environment where it is not wanted [34,35], or otherwise
- Increasing harmful effects to non-target plants [36,37] and aquatic species [38,39]

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2. Historical background

The history of adjuvants in agriculture dates back to the 18th and 19th centuries when additives such as resins, tar, flour, molasses, and sugar were used with lime, sulfur, copper or arsenates to improve adherence and biological performance of active ingredients by modifying the physicochemical properties of the spray solution [40].

The first agricultural adjuvant was a soap solution (Gillette 1888, 1890) (cit. by Hazen, [41]). Soap solutions and kerosene were used in the United States to kill insect eggs or were added to arsenical solutions to increase toxicity to weeds [42]. Animal oil soaps were common adjuvants in use before 1900, as well (Gillette1889) (cit. by Hazen, [41]). They were derived from animals, fish, and whale oil and were used to enhance the pesticide performance. Sugars and glue were considered as stickers and many other materials followed as adjuvant research continued [43].

The modern era of synthetic organic pesticides began in the 1930s. The research behind medical (including antibiotics) and military uses funded research that led to the discovery of many pesticide families that are still in use today. An initial breakthrough in weed control occurred with the introduction of 2,4-D in the 1940s for broad-spectrum broadleaf weed control in corn and cereal crops [44]. Soaps and mineral oils were replaced by nonionic surfactants. Nitrogen fertilizers like ammonium sulfate (AMS) and urea ammonium nitrate (UAN) were also used to enhance the herbicidal activity while glycerin was introduced as humectant.

In the 1960s and 1970s, modern types of adjuvants such as crop oil concentrates (COC) were developed, which were used to reduce doses of atrazine and to lower spray volumes. Organosilicone-based adjuvants, nonionic surfactants (NIS), which have excellent wetting and spreading capability and enhance the penetration of post-emergent herbicides, were developed later [45].

3. Classification of adjuvants

There are over 3,000 adjuvants available for use. These can be grouped into three general types:

- Activators,
- Spray modifiers and
- Utility modifiers

4. Activators

Activators modify certain herbicide characteristics, including particle size and viscosity of the herbicide spray, evaporation rate, etc. Usually, they increase herbicide activity, herbicide spread, absorption into plant tissue, and rainfastness, and decrease photodegradation of the herbicide.

There are three categories of activators: surfactants, wetting agents, and oils.

4.1. Surfactants (SURFace ACTive AgeNTS)

Surfactants (SURFace ACTive AgeNTS) are a type of activators designed to improve the dispersing/emulsifying, absorbing, spreading, wetting, sticking, and/or penetrating properties of the spray mixture [6]. Surfactants primarily influence the ability of herbicides to penetrate the leaf's waxy cuticle. Most herbicides are prepared in a solution of water. Water is a chemically polar material and thus can be repelled by the waxy surface of leaves. Water containing a surfactant reduces the surface tension of water on plants, spread in a wet thin layer over a waxy leaf surface, and allow the herbicide formulation to enter into the plant.

Surfactants can be classified in four groups on the basis of the ability to ionize the aqueous solution. Those groups are:

- Nonionic — are the most commonly used in agriculture and can be mixed readily with any herbicide. They produce little or no ionization in water (no electrical charge). Organosilicone and silicone surfactants are two types of nonionic surfactants.
- Cationic — are not often used with herbicides. They have a positive charge,
- Anionic — rarely used with herbicides, but mainly used in cosmetics, household cleaners, many domestic detergents, etc. They have a negative charge, and
- Ampholytic (amphoteric) — have a both positive and negative charge, that is, in aqueous solution are capable forming cations or anions.

4.2. Wetting agents

Wetting agents increase the ability of water to displace air or liquids from the leaf surface, allowing it to be wet by the herbicide. Wetting agents help spread the solution more evenly over the leaf.

4.3. Oils

Oils increase the retention time of a solution on leaves, allowing for an increase in herbicide uptake. Oils mostly contain emulsifiers to allow them to mix with water. Some claims regarding oils include reduced rainfast periods, more uniform droplet size (drift reduction), less spray evaporation, and better penetration of herbicide into waxy leaves.

All oils are basically mineral oils with different contents of surfactant in formulation (3%--20%). They can be classified as:

- Crop oils
- Dormant oils

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- Crop oil concentrates
- Vegetable oils
- Vegetable oil concentrate
- Modified vegetable oil, and
- Modified vegetable oil concentrate

4.3.1. Crop oils

Crop oils are emulsifiable petroleum oil-based products containing up to 5% w/w surfactant and the remainder of phytobland oil.

4.3.2. Dormant oils

Dormant oils are horticultural spray oils applied during the dormant phase of the targeted plant [2]. There are ''quick-break'' or dormant oils that use a very low amount (2%--5%) of emulsifier for dispersion into the spray tank [41].

4.3.3. Crop Oil Concentrates (COC)

COC are the most commonly used oils in agriculture. They were introduced to the market in the 1960s [45]. COC are emulsifiable petroleum oil-based products containing 5%--20% w/w surfactant and a minimum of 80% w/w phytobland oil [2]. COC enhanced activity of aryloxyphenoxy propionates, cyclohexadinones, triazines, phenoxy acid urea herbicides, imidazolinones, etc. [46,47,26].

4.3.4. Vegetable oils

Vegetable oils are also used as herbicide adjuvants. The base in formulation is oil from sunflower, soybean, oilseed rape, peanut, or corn, which is combined with surfactants in different content.

4.3.5. Vegetable oil concentrates

Vegetable oil concentrates are emulsifiable vegetable oil products containing 5%--20% w/w surfactant and a minimum of 80% w/w vegetable oil [2]. There are some vegetable oil concentrates used in the same manner as the crop oil concentrates, typically based upon canola or soybean oil, using 5%--10% emulsifier for dispersion [41].

4.3.6. Modified vegetable oil

Modified vegetable oil is oil extracted from seeds that have been chemically modified. Methylated seed oils (MSO) are vegetable oils mainly from oilseed rape or sunflower esterified with alcohol ethanol to get methyl esters.

4.3.7. Modified vegetable oil concentrate

Modified vegetable oil concentrate is an emulsifiable, chemically modified vegetable oil product containing 5%--20% w/w surfactant and remain chemically modified vegetable oil. Some of the best vegetable-based products are those modified (derivatized) to methyl and other lower alkyl esters such as methylated soybean oil, methyl sunflowerate, or ethyl canolate.

5. Spray modifiers

Spray modifiers affect the delivery and placement of the spray solution. They confine or alter the physicochemical characteristics of the spray solution [48], and make the herbicide spray easier to aim, reduce herbicide drift in the air, and cause the spray to more readily adhere to the plant. Spray modifiers include:

- Thickening agents (i.e., invert emulsions and polymers)
- Stickers
- Spreaders
- Spreader-stickers
- Foaming agents
- Humectants, and
- UV absorbents

5.1. Thickening agents

Thickening agents modify the viscosity (thickness) of spray mixtures. They control drift or slow evaporation after the spray has been deposited on the target area. Slowing evaporation is important when using systemic herbicides, because they can penetrate the plant cuticle only as long as they remain in solution. Invert emulsions, polymers, and *drift control agents* are three types of thickening agents commonly used in herbicide applications.

5.1.1. Invert emulsions

Invert emulsions are mixtures of inverting oil and water, having a mayonnaise-like appearance on the water surface and a snowflake-like appearance under the water surface. Depending on their solubility, herbicides dissolve in either the oil or water component. The oil in the case of *invert emulsions* reduces the evaporation, produces bigger particles, reduces drift problems and can be sprayed on wet foliage [49].

5.1.2. Polymers

Polymers are a very large, chain-like carbon molecules made up of monomers, up to 40,000 carbons in length, forming a thick mucus-like material which helps to break the surface tension of water and enhance sinking of herbicides [50,51].

5.1.3. Drift control agents

Drift control agents modify spray characteristics to reduce spray drift, usually by minimizing small droplet formation. They are generally polyacrylamide or polyvinyl polymers [52].

5.2. Stickers

Stickers assists the spray deposit to adhere or stick to the the leaf surface and may be measured in terms of resistance to time, wind, water, mechanical action, or chemical action [2]. Stickers may be heavy petroleum fractions, water-soluble polymers, acrylic latex, epoxidized seed oils (similar to boiled linseed oil, which dries on exposure to air), or alkylphenol condensates called resins. Stickers are commonly used in field crops (like corn and soybeans) where residue on leaves is not a problem. They are usually used for application of fungicides and insecticides rather than herbicides.

5.3. Spreaders

Spreaders are compounds that cause the surface tension of the herbicide to be reduced in such a way that it easily spreads into a very thin film over a leaf surface. Spreaders increase the efficiency of the herbicide dramatically. Typically, the alcohol ethoxylates [53] such as tridecanol ethylene oxide allow a spread diameter increase of two to three times. They may contain fatty acids, latex, aliphatic alcohols, crop oils such as cottonseed, or inorganic oils.

5.4. Spreader-stickers

Spreader-stickers are essentially combinations of stickers and spreaders. They provide additional retention of herbicide in wet conditions. They are usually used with contact insecticides and fungicides for which complete coverage is critical.

5.5. Foaming Agents

Foaming Agents are compounds that facilitate formation of foam for reducing drift and evaporation. These agents are used infrequently for drift control of herbicide applications.

5.6. Humectants

Humectants, like stickers, increase the amount of time that the herbicide is on the leaf, in a form available for uptake [41]. When water evaporates from the spray droplet and the herbicide becomes a crystalline residue, it is no longer available for uptake into the leaf. Humectants keep the spray deposit moist and in true solution, and therefore extend the time that it is available for absorption [54].

5.7. UV absorbents

UV absorbents protect herbicides from the deleterious effect(s) of sunlight. They may do this by either physical or chemical processes, such as by increasing the rate of herbicide uptake into the cuticle, or by absorbing the UV-light themselves.

6. Utility modifiers

Utility modifiers help minimize handling and application problems. They do not directly improve efficacy, but widen the conditions when an herbicide can be used or maintain the integrity of the spray solution. For example, utility modifiers reduce foaming, increase solubility, modify pH, or reduce spray drift.

Types of modifiers include emulsifiers, dispersants, stabilizing agents, coupling agents, co-solvents, compatibility agents, buffering agents, antifoam agents, and ammonium fertilizers.

6.1. Emulsifiers

Emulsifiers are molecules with one hydrophilic and one hydrophobic end. They make it possible for water and oil to become finely dispersed in each other, creating a stable, homogeneous, smooth emulsion. Most crop oils contain emulsifiers to allow them to mix with water and some contain various levels of surfactants.

6.2. Dispersants

Dispersants are chemicals that are sprayed on a surface oil slick to break down the oil into smaller droplets that more readily mix with the water. These water soluble dispersants have been found to be unique and highly effective dispersants for water insoluble agricultural suspension concentrate formulations.

6.3. Stabilizing agents

Stabilizing agents act as thickening or gelling agents that increase the viscosity of the final product. These agents stabilize emulsions, either by adsorbing to the outer surface of oil droplets. Stabilization can be achieved in agricultural suspension and emulsion through the use of fine-particle-size solids and fine liquid droplets in the disperse phase along with appropriate dispersants and wetting agents.

6.4. Coupling agents

Coupling agents are compounds which provide a chemical bond between two dissimilar materials, usually an inorganic and an organic. Organosilanes are well-suited in this application because of the ability to incorporate an organic-compatible functionality and an inorganic-compatible functionality within the same molecule.

6.5. Cosolvents

Cosolvents are defined as water-miscible organic solvents that are used in liquid herbicide formulations to increase the solubility of poorly water-soluble substances or to enhance the chemical stability of an herbicide.

6.6. Compatibility agents

Compatibility agents allow simultaneous application of two or more ingredients. They are most often used when herbicides are applied in liquid fertilizer solutions.

6.7. Buffering agents

Buffering agents are used to change the pH and hardness of the water and to increase the dispersion or solubility of herbicides in alkaline or acid waters used in making up an herbicide solution. Ammonium sulfate (AMS) is sometimes added to reduce hard water problems.

6.8. Antifoam agents

Antifoam agents reduce foaming in spray mixtures that require vigorous agitation. They are particularly useful in soft water. Antifoam agents are usually siliconebased and used at 0.1% or less of the total spray volume [55].

6.9. Ammonium fertilizers

Ammonium fertilizers are often added to spray solutions with foliar applied herbicides. The two most common ammonium fertilizers used are ammonium sulfate (AMS) and urea ammonium nitrate (UAN) solution (28-0-0). The exact mechanism of action for ammonium fertilizers is not known although increased herbicide uptake into plant has been reported [26].

7. Positive interaction between herbicide efficacy and adjuvants

Surfactants are the most widely used and probably the most important of all adjuvants [56]. They can be especially effective in improving the biological activity of many herbicides [57-59]. Nonionic surfactants (NIS) improved the effect of nicosulfuron [58] and enhanced glyphosate absorption, which was 20 times greater and the spread of spray drop was 200 greater than with no adjuvants added [60].

Several researchers have observed that adjuvant efficacy is dependent on the herbicide being applied and the characteristics of the target weed species [61-63]. For example, MSO increase foliar absorption and efficacy of many herbicides, including primisulfuron, rimsulfuron, imazethapyr, quinclorac, and several graminicides for grass weed control [21,64-66]. MSO was the only adjuvant used with foramsulfuron that provided acceptable giant foxtail control (*Setaria faberi*) [32]. Stagnari *et al*. [67] found strong influence of mineral and vegetable oil on clodinafop-propargyl and diclofop-methyl + fenoxaprop-p-ethyl on *Lolium multiflorum*, *Avena ludoviciana*, and *Phalaris minor*.

NIS have been effective in improving the activity of several sulfonylurea herbicides, including primisulfuron, rimsulfuron, and thifensulfuron, as well [57,58,68]. MSO and COC have been shown to further enhance the effectiveness of several herbicides on certain weed species, including nicosulfuron [23]. These adjuvants enhanced the effectiveness of chlorimuron and imazethapyr on purple nutsedge (*Cyperus rotundus* L.). Chlorimuron controlled *Cyperus rotundus* more effectively with COC than with a NIS or organosilicone surfactant (OSS), but imazethapyr was more effective with OSS or COC than NIS [24]. Seed-oil-based crop oils and organosilicone adjuvants combined with halosulfuron provided 100% control of *Cyperus rotundus* L. 8 weeks after treatment (WAT) compared with <90% control when halosulfuron was combined with the nonionic or paraffin-based crop oil adjuvants [69]. Similar results were found in studies of McDaniel *et al*. [70] who reported that >90% control of yellow nutsedge (*Cyperus esculentus* L.) in container landscape plants was achieved with late-spring applications of halosulfuron at 18 g/ha combined with 0.5% (v/v) rate of either the soybean crop oil Scoil®, or the sunflower *(Helianthus annuus* L.) crop oil Sun-It II. Increased control with nicosulfuron on yellow foxtail [*Setaria glauca* (L.) Beauv.] and large crabgrass [*Digitaria sanguinalis* (L.) Scop.] with MSO compared with other oils and surfactant adjuvants has been reported by Nalewaja *et al*. [23]. Young and Hart [71] reported that isoxaflutole applied with MSO provided greater giant foxtail (*Setaria faberi* Herrm.) control compared with isoxaflutole applied with NIS or COC. The addition of an organosilicone (OSL) adjuvant to primisulfuron spray solution increased foliar herbicide absorption, spray retention, and control of *Setaria faberi* Herrm. compared with adding a NIS to the spray solution [21].

The addition of AMS or UAN to the spray solution can enhance herbicide effectiveness by further increasing herbicide absorption [26,72] which gives better result up to 12%--13.5% than use of herbicide alone [73]. For instance, thifensulfuron absorption into velvetleaf (*Abutilon theophrasti* Medicus) was increased from 4% to 45% when 28% UAN was added to the spray solution [61,74,75]. Addition of AMS and potassium phosphate to the spray solutions of MSMA and dalapon enhanced control of *Sorghum halepense* (L.) Pers. and *Cyperus rotundus* L. [76,77]. Wills [78] reported that AMS and potassium phosphate each increased the phytotoxicity of glyphosate. Wills and McWhorter [79] further reported that the monovalent cations NH_4^+ and K^+ in combination with anions including NO_3^-, Cl^-, and CO_3^{2-} increased the phytotoxicity of glyphosate. Glyphosate isopropylamine, bentazon sodium, 2,4-D dimethylamine, and dicamba sodium were all equally effective when AMS was added to the spray tank before or after the herbicide. The benefit of AMS in enhancing herbicide efficacy was greatest when used with spray water high in cations [80]. Also, several studies have indicated that AMS may be used to overcome an antagonism between two herbicides [81,82]. The antagonism between bentazon and sethoxydim was overcome with the addition of AMS and by changing the adjuvant from a COC to a highly concentrated oil-based adjuvant [83,81]. Applying UAN (0.4 or 0.8 g/ha) and organosilicone-based nonionic surfactant (OSL/NIS) or methylated seed oil/ organosilicone (MSO/OSL) adjuvant with bispyribac enhanced efficacy and reduced the time period required to affect bispyribac efficacy on barnyardgrass [*Echinochloa crus-galli* (L.) Beauv] [84]. Bunting *et al*. [32] reported 90% or greater giant foxtail (*Setaria faberi* Herrm.) control with the addition of MSO or MSO plus 28% UAN. Twenty percent control of giant foxtail was obtained when a COC or a NIS was added to foramsulfuron, whereas control increased to 90% and 85%, when 28% UAN was added to COC or NIS, respectively. Density, fresh and dry weight of *Trianthema portulacastrum, Cyperus rotundus* and *Coronopus didymus* 20 and 40 days after sowing and at harvest of maize decreased significantly when foramsulfuron + isoxadifen-ethyl was applied at 1125 g/ha a.i. plus 3% UAN solution as adjuvant as compared to herbicide

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alone. Finally, UAN used as an adjuvant reduced the herbicide dose up to 10% without compromising maize yield loss due to weeds [85]. Considering the wide-spread use of tribenuron-methyl, the identification of the most appropriate adjuvant for tribenuron-methyl against different weed species was found to be necessary [86]. The activity of tribenuron-methyl was significantly enhanced by NIS (20% isodecyl alcohol ethoxylate plus 0.7% silicone surfactants), an anionic surfactant (25.5% alkylethersulfate sodium salt), and a vegetable oil (95% natural rapeseed oil with 5% compound emulsifiers) on *Sinapis arvensis, Tripleurospermum inodorum, Papaver rhoeas*, and *Chenopodium album*, and only minor differences were observed among the tested adjuvants [87]. Besides sulfonylureas, an addition of adjuvants greatly improved the efficacy of saflufenacil, a new PPO-inhibited herbicide. For example, ED_{90} values for field bindweed (*Convolvulus arvensis* L.) control at 28 days after treatment (DAT) were 71, 20, 11, and 7 g/ha for saflufenacil applied alone, or with NIS, COC, or MSO, respectively. MSO was the adjuvant that provided the greatest enhancement of saflufenacil across all broadleaf weed species tested — *Taraxacum officinale, Convolvulus arvensis, Thlaspi arvense, Lamium amplexicaule, Lactuca serriola*, and *Capsella bursa-pastoris* [88]. Murphy *et al*. [89] investigated the influence of different adjuvants on flamprop-M-isopropyl efficacy in controlling of *Avena* spp. The mean results from six trials (five wheat, one barley) showed that the addition of adjuvants, “Swirl” and “Dobanol 25–7” was beneficial, increasing wild oat floret control from a mean value of 80% to 92% at current recommended rates (flamprop-M-isopropyl, 600 g/ha; “Swirl,” 2.5 L/ha). However, combinations of flamprop-M-isopropyl and “Dobanol 25-7” gave superior levels of control even at lower a.i. application rates. For example, a mean level of 96% control of *Avena* spp. was obtained at 300 g/ha a.i. with 1200 g/ha “Dobanol 25-7”; with even better control at higher rates of application of both components.

8. Interaction between herbicide absorption/translocation and adjuvants

Considering environmental factors, rain shortly after an herbicide application is one of the most detrimental issues for herbicide performance. Adjuvants have been shown to improve the rainfastness of herbicides and the effect on rainfastness should be considered when selecting an adjuvant [90,91]. A number of studies have been published that outline the beneficial effects of OSL adjuvants in reducing the critical rain-free period after the foliar herbicidal application. Field and Bishop [92], Reddy and Singh [93], and Roggenbuck *et al*. [63] reported that the addition of an OSL adjuvant to glyphosate reduced its critical rain-free period. The reduction of the critical rain-free period was attributed to decreased liquid surface tension of glyphosate caused by the OSL adjuvant and subsequent promotion of stomatal infiltration of glyphosate into the plant.

Studies with ^{14}C-labeled glyphosate have demonstrated that plants absorb as little as 22% of the amount applied; however, the addition of surfactant improved absorption up to 35% [94]. For instance, the OSL adjuvants produced rapid absorption of the ^{14}C-glyphosate into the redroot pigweed (*Amaranthus retroflexus* L.) leaves, reaching maximum absorption within 0.5–1.0 h after application (HAT). The conventional adjuvants produced slower absorption of the ^{14}C-glyphosate, as the maximum absorption was not achieved until at least 24 HAT in redroot pigweed, remaining similar until 72 h [60]. Non-silicone surfactant (NSS) "Browndown" increased the speed and quantity of glyphosate uptake, with no adverse effects on herbicide translocation. At the recommended rate (0.25% v/v), this surfactant reduced spray retention compared to OSS, "Pulse" (0.1% v/v), but provided faster brown-out of foliage and equivalent herbicide efficacy on glyphosate-tolerant ryegrass (*Lolium perenne* L.) in spring [95]. Surfactants of higher ethylene oxide (EO) content provided greater uptake enhancement in wheat, broad bean, and common lambsquarters for glyphosate, whereas those of lower EO content were more beneficial for 2,4-D uptake [96]. Addition of the water conditioning agent Quest (0.25% v/v) to glyphosate spray mixtures diminished the influence of simulated rain events following glyphosate application [97]. OSS increased rainfastness of primisulfuron on velvetleaf (*Abutilon theophrasti* Medicus) more than other adjuvants, although no differences in velvetleaf control occurred under rain-free conditions [98]. NIS (20% isodecyl alcohol ethoxylate plus 0.7% silicone surfactants), an anionic surfactant (25.5% alkylethersulfate sodium salt), and a vegetable oil (95% natural rapeseed oil with 5% compound emulsifiers) significantly improved the rainfastness of tribenuron-methyl on *Tripleurospermum inodorum*, with differences among the adjuvants being more pronounced when rain occurred shortly after herbicide application. The effect of the vegetable oil on tribenuron-methyl's rainfastness was significantly lower than that of the surfactants with rain at 1 HAT, while no significant differences among the three adjuvants were observed when rain occurred at 2 and 4 HAT [87]. The addition of UAN decreased the rainfast period from 8 h (registered rainfast period) to 1 or 4 h (99 to 100% control) when either the between bispyribac application and wash-off during a rainfall event [84].

In contrast to surfactants, water repellent adjuvants increase surface tension, thus inhibiting wetting of the leaf surface. The water repellent DC 1-6184 may have some utility for reducing corn injury when isoxaflutole is applied to corn foliage at early growth stages [99]. These results are consistent with the observation of Nelson and Penner [100] that DC 1-6184 applied in combination with herbicide safener R-29148 and isoxaflutole reduced injury to spike-stage corn (28%) as compared with isoxaflutole applied alone (53%) or isoxaflutole applied with only R-29148 (37%). Penner and Fausey [101] found that DC 1-6184 consistently reduced retention of flumioxazin spray on plant foliage by increasing the number of droplets that bounced off the foliage. Flumioxazin spray had the greatest retention of all herbicide treatments on tomato when DC 1-6184 was included. Also, the same water repellent, DC 1-6184, reduced isoxaflutole retention on tomato, wheat, and cabbage [100].

9. Interaction between herbicides, environment, and adjuvants

From an environmental aspect, adjuvants can weakly bind herbicides and release them slowly in order to prolong the efficacy of herbicides and to minimize their leaching into groundwater. Enersol 12% adjuvant resulted in a 13%–18% reduction in leaching of dicamba and bromacil in five pore volumes of leachate. The leaching of simazine was significantly decreased when charcoal, three humic substances (Enersol SP 85%, Enersol 12%, and Agroliz), and a synthetic polymer (Hydrosorb) were used. However, the decrease in leaching was significantly greater when using Enersol SP 85% or Enersol 12% (24%–28%) than when using the other adjuvants

(12%–16%) [30]. In a study by Locke *et al*. [102] nonionic, cationic, and anionic adjuvants generally increased the water solubility of cyanazine, atrazine, and norflurazon (10%--91%). Cyanazine and atrazine sorption (K_d) was reduced in most soils with nonionic adjuvant (ranged 1.18--4.50 and 1.59--4.28, respectively) compared with water alone (1.36--5.59 and 1.75--4.59, respectively), whereas norflurazon sorption was increased with nonionic adjuvant (ranged 3.88--8.76 in water; 4.66--9.82 in adjuvant). Similarly, more cyanazine and atrazine were desorbed by solutions containing adjuvant than in water, indicating that adjuvants may be useful in remediating some soils contaminated with certain herbicides.

10. No or negative interaction between herbicides and adjuvants

In many situations, as mentioned earlier, adjuvants can significantly enhance an herbicide's effect [25]. However, it is important to note that in some circumstances, adding adjuvants will not significantly improve control. For example, several studies have shown that the addition of AMS to herbicides increases the control of *Abutilon theophrasti*; however, control of other species, such as *Chenopodium album* is not always improved [74, 75,103]. Leafy spurge (*Euphorbia esula* L.) control with annual picloram or picloram plus 2,4-D treatments was similar whether applied alone or with a variety of adjuvants in the field [104]. Addition of laffmul DA and ethoxylated castor oil (EO 40) – both nonionic crop oil concentrates surfactants reduced the efficacy of glufosinate ammonium and 2,4-D Na salts in controlling of *Cyperus rotundus* and *Oxalis latifolia* [105]. Addition of sulfuric acid and/or of AMS to spray solution does not increase herbicide activity of glyphosate [106]. This claim is corroborated by results of Breeden *et al*. [107] who reported that AMS additions to glyphosate, while not decreasing effectiveness, did not improve efficacy over glyphosate applied alone to sicklepod [*Senna obtusifolia* (L.) Irwin and Barneby]. The addition of two polysaccharide adjuvants decreased the percentage of the spray volume in small diameter spray droplets (<141 mm) and either had no effect or increased glyphosate efficacy [108]. One disadvantage to the use of surfactants with glyphosate is the postapplication effect. Surfactants tend to reduce the translocation efficiency of glyphosate within the plant [94]. Studies with water-stressed plants have shown that surfactants do enhance absorption, even under stress, but they decrease movement of the herbicide once it is inside the plant tissue [94]. Glyphosate application rate was more important than adjuvant addition or sprayer type, with the higher rates of application providing greater control [109].

Sometimes adjuvants can decrease the killing power of the herbicide (antagonistic effects). The efficacy of sethoxydim or clethodim on large crabgrass [*Digitaria sanguinalis* (L.) Scop.] was antagonized by the addition of halosulfuron with NIS or COC. Simalarly, combinations of sethoxydim and halosulfuron with COC or MSO were antagonistic on smooth crabgrass (*Digitaria ischaemum* Schreb. ex Muhl.) [33].

Some adjuvants can increase harmful effects to non-target plants. Imazamox applied at 108 g/ha plus 1% (v/v) MSO applied in the fall consistently injured all wheat cultivars more than the same rate with NIS at 0.25% and 54 g/ha imazamox regardless of adjuvant and timing [37]. Injury caused by these treatments ranged from 23%to 70% for all cultivars. Adjuvant affected cotton injury from CGA 362622. NIS resulted in increased cotton injury at 29%, whereas COC increased cotton injury to 37%. [110]. Crooks *et al*. [111] reported similar injury from CGA 362622 with either NIS or COC. Flumioxazin did not injure wheat or cabbage except when the silicone adjuvant was added, which increased retention of the spray solution [112].

Sometimes adjuvants can have negative effects, such as increasing the formulation's ability to spread or persist in the environment where it is not wanted. According to Kucharski and Sadowski [113], the addition of adjuvants caused an increase of the residues of active ingredients in the soil and roots of sugar beet compared to plots with a reduced dose of herbicide without adjuvants. Swarcewicz [114] and Swarcewicz *et al.* [34] described experiments in which influence of adjuvants on trifluralin degradation were tested. 50 DAT residues of trifluralin amounted to 38% of initial dose and in treatments with adjuvants residues ranged from 42% to 49% of initial dose. In a similar experiment Kucharski [35] also proved that the addition of adjuvants slowed down the degradation and increased the level of phenmedipham residue in the soil. Some adjuvants can have adverse effects on aquatic species, and certain types can be extremely toxic to fish and shellfish [39]. Parr [38] reports that some adjuvants caused noticeable alterations in fish gill tissue, and that the toxicity of these adjuvants increased as exposure time increased.

11. Conclusion

The agricultural adjuvants market, in terms of value, is projected to reach $3,183.04 million by 2019, at a CAGR of around 5.6% from 2014 [115]. Numerous factors such as, easy application, modern production practices, new product offerings, increased availability, increasing infestation of pests and diseases, and government regulations to protect the environment from hazardous chemical usage are the major drivers of the agricultural adjuvants market. Adjuvants are quietly helping to revolutionize the agrochemical business as they are the best tools for farmers to improve application, facilitate the right dosage, and achieve more cost-effective, better targeted, and environmentally acceptable pest control. Agricultural adjuvants play an essential role in the performance of most herbicides, fungicides, and insecticides, and function by transforming the dosage from preventative, high-dose applications to low dosages, specifically targeted for curative applications.

From all previous research mentioned, it can be concluded that the herbicide-adjuvant--plant-environment interaction is a complex system. Understanding the different roles of adjuvants in the behavior of herbicides is essential for their optimum utilization. Adjuvants can improve the biological activity of the herbicide active ingredient, the performance of the spray application, and the economics of herbicide applications, but in some circumstances adjuvants can manifest negative effects. Therefore, there is no universal adjuvant that can improve the performance for all herbicides, against all weeds, or under all environmental conditions. The herbicide and adjuvant selected and the relative amounts used must be tailored to the specific conditions of each application.

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