

# Adjuvants with Herbicides

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## Adjuvants

- Surfactants
- Oils
- Salts – AMS, AMN + UREA, BUFFERS
- Antifoam
- Drift reduction

## Surfactants

**Spray retention** – droplet size, spray volume, plant species, dynamic surface tension, HLB all interact in determining spray retention.

Redroot pigweed retained spray without surfactant and surfactant reduced retention with high spray volumes.

Common lambsquarters spray retention was increased by adjuvants: low HLB surfactant > high HLB surfactant > methylated vegetable oil > vegetable oil = petroleum oil.

Low spray solution dynamic surface tension generally relates positively to spray retention. Low surface tension is mainly important for retention of large spray droplets on hard to wet species.

**Herbicide absorption** – surfactant HLB, deposit characteristics, surfactant concentration all directly or indirectly determine herbicide absorption.

Absorption of water soluble herbicides generally is enhanced more by surfactants with high HLB, hydrophilic, than low HLB, lipophilic surfactants.

Nonspreading surfactants that leave a concentrated spray deposit also appears positive to enhancement of water soluble herbicides.

Oil soluble herbicides formulated as emulsifiable concentrates are not greatly influenced by surfactants. The formulant may provide the needed solvents for absorption or the parent oil characteristics of the herbicide alone may directly penetrate the plant epicuticular surface.

## Oils

**Absorption** – oil adjuvants function by enhancement of herbicide absorption. Glyphosate (Roundup) and paraquat (Gramoxone) which are very water soluble are antagonized

by oil adjuvants. However, other herbicides formulated as water soluble salts (bentazone, dicamba, 2,4-D) are often enhanced by oil adjuvant. The solubility of the parent herbicide acid may be more important than the formulated soluble salt. The final molecular form in the spray deposit may not be that of the formulated salt with different solubility.

Methylated vegetable oils are far better solvent of cuticular wax than either the parent vegetable oil or petroleum oils. The methylated vegetable oils appear most effective with herbicides having intermediate water solubility (nicosulfuron, sethoxydim, clethodim). The very lipophilic herbicides (diclofop, quizalofop, fluazifop) are similarly enhanced by methylated vegetable or petroleum oil. Quizalofop is antagonized by vegetable oil. The above interaction between oil types and herbicides indicates that certain herbicides require the solubilization from the methylated vegetable oil, but other more lipid soluble herbicides may penetrate the cuticular wax without an oil. The presence of an oil is still required to provide a micro environment for absorption. The antagonism of quizalofop by vegetable oil may be from too great of an affinity of quizalofop for the oil preventing absorption.

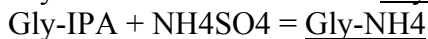
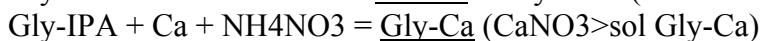
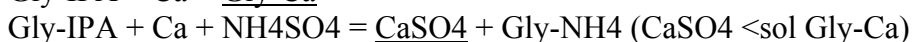
## **Salts**

### *Overcome antagonistic salts in the spray solution*

Glyphosate and weak acid type herbicides in spray carriers high in certain cations (Ca, Na) combine with these cations upon droplet drying to form less absorptive compounds. Ammonium and sulfate ions either directly or indirectly prevent the formation of the less absorptive forms. The ammonium ion by mass action may form an ammonium herbicide salt positive to absorption. The sulfate ion causes formation of the relatively insoluble calcium sulfate early in droplet drying preventing the calcium from subsequent combination with the herbicide.

Glyphosate salt model:

Compound solubility, gly IPA & Na = 50%; glyH4 = 30%; glyCa = 3%



The above equations indicate the form of glyphosate that occurs in the dry spray deposit because of solubility of various ion combinations. The underlined compounds are those to first precipitate as concentration increases upon droplet drying. Note that ammonium nitrate overcomes sodium but not calcium ions in the spray carrier, but ammonium nitrate overcomes sodium antagonism. In the case of sodium the ammonium ion is the functional ion. However, when calcium is present the sulfate (phosphate also effective) ion is required to remove the

calcium before it combines with glyphosate. The deposit form of glyphosate is important to absorption and efficacy as indicated below.

### Glyphosate salt efficacy applied with X-77 and absorption with MON0818

Glyphosate salt	% fresh wt. reduction	Absorbed, % of applied
Sodium	18	21
Ammonium	33	44
Isopropylamine	39	44
Calcium	11	1
Acid	37	49
LSD 5%	5	5

Other weak acid herbicides formulated as salts would have a similar response to salts. However, the solubility of the parent compound could change the salt solubility interrelationships. Below are results of salt antagonism of several herbicides and response to ammonium sulfate.

### Kochic (%FWR) with herbicides, formulations, and salts

Herbicide	-----Carrier salt-----		
	None	CaCl <sub>2</sub>	CaCl <sub>2</sub> + AMS
2,4-D dea	45	0	45
2,4-D Na	0	0	38
Bentazon-Na	55	7	61
Dicamba-dma	67	17	70
Dicamba-Na	34	9	69
Acifluorfen	100	48	100
Glyphosate-IPA	100	4	24
LSD 5%	-----		

In the above table ammonium sulfate did not overcome the calcium antagonism of glyphosate. All treatments were without a surfactant and result of other research indicated that surfactant was essential to overcoming calcium chloride antagonism of glyphosate for kochia. The salts in the deposit on the crystalline wax of the kochia leaf probably prevent good physical contact by glyphosate with the epicuticular surface. The presence of a surfactants provides a liquid route for glyphosate diffusion and absorption. Thus, the amount of salt and physical characteristics of the deposit could influence herbicide efficacy. Salts that upon drying give large crystals may deposit above the herbicide and surfactants and not interfere with absorption. On the other hand, salts that leave a powder type deposit could physically trap the herbicide, reducing absorption.

The effectiveness of various herbicide forms appears to depend upon environment. Sodium salt forms of some herbicides were effective under moist conditions (dew or high

humidity), but not when dry. Thus, the beneficial response with some herbicides from the presence of ammonium salts in the spray solution depends on the prevailing conditions.

***Direct responses to ammonium fertilizers***

Ammonium fertilizers have enhanced efficacy of herbicides in the absence of antagonistic salts. Possible reasons for these enhancements are increased plant growth, overcoming antagonistic salts within the plant, changing spray deposit characteristics and stimulation of the proton gradient by ammonia at the cell membrane level. Ammonium sulfate and some other fertilizer salts have enhanced phytotoxicity of glyphosate to sunflower and acefluorfen to velvetleaf in the absence of any antagonistic ions in the spray solution. The Table below indicates species response to glyphosate and salts.

**Species percent FW reduction from glyphosate with salts**

Species	-----Salts-----			
	None	CaCl <sub>2</sub>	AMS	Ca+AMS
Wheat	62	0	69	74
Sunflower	55	1	100	93

The enhancement of glyphosate phytotoxicity to sunflower by ammonium sulfate in a spray solution without antagonistic salts is a direct benefit from the ammonium sulfate. Micrographs of the spray deposits indicated the presence of crystals resembling Ca SO<sub>4</sub>. Thus, it was speculated that the calcium from the plant may have been removed from complexing with glyphosate.

Nitrogen fertilizers applied with herbicides may be positive to plant growth needed for a toxic response. Research in the late 1960's had shown that 28% nitrogen fertilizer in a barban spray overcame the tolerance in wild oat that occurred with plant growing in soil with low fertility. Barban was an emulsifiable formulation that should not have been antagonized by spray carrier salts. The response may have been a growth response or an increased cellular membrane penetration as reported for imazethapyr (see Figure).

***Indirect response to fertilizer salts***

Nitrogen fertilizers in combination with oils in spray solution have overcome the antagonistic effects of the oil with glyphosate. The speculation is that the fertilizer salts create micro hydrophilic areas with the spray deposit containing a high concentration of the highly water soluble glyphosate giving increased absorption and efficacy.

Spray deposits are the final step in determining herbicide penetration into the leaf. Salts depending on their physical and chemical characteristics influence droplet spread; deposit physical appearance; and deposit hydrophilic and lipophilic characteristic. The optimum HLB of surfactants for some herbicides is lower when the spray contained fertilizers. This is believed from the fertilizer reducing spread of the low HLB surfactant important to absorption of water soluble herbicides. Fertilizer with high HLB surfactants reduced efficacy by causing a bulky

deposit with poor contact to the epicuticular surface. Fertilizer and salt influence on herbicide efficacy differs with both the salt and surfactant which may be from within deposit herbicide – salt – solubility relationships.

***Questions relative to nitrogen adjuvants***

- Amount and efficacy, percentage vs area
- Surfactant fertilizer mixtures
- Type of nitrogen compound
  - AMS, AMN, UREA, AMCitrate, Amphosphates
  - Importance of nitrogen vs any salt
- Drift reduction compounds and fertilizers
- Function of nitrogen compounds, physiological or physical
- Pesticides responding to fertilizer salts.

**Postemergence Herbicide Action**

