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Spray adjuvants: The rest of the story

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Introduction

Questions about adjuvant selection are common. Adjuvants are not regulated by the EPA or any other regulatory agency allowing an unlimited number of adjuvants. Adjuvants are composed of a wide range of ingredients which may or may not contribute to herbicide phytotoxicity. Results vary when comparing specific adjuvants, even within a class of adjuvants. POST herbicide effectiveness depends on spray droplet retention, deposition, and herbicide absorption by weed foliage. Adjuvants and spray water quality (Paragraph A6) influence POST herbicide efficacy. Adjuvants are not needed with PRE herbicides unless weeds have emerged and labels include POST application.

Spray adjuvants generally consist of surfactants, oils and fertilizers. The most effective adjuvant will vary with each herbicide, and the need for an adjuvant will vary with environment, weeds, and herbicide used. Adjuvant use should follow label directions and be used with caution as they may influence crop safety and weed control. An adjuvant may increase weed control from one herbicide but not from another. To compare adjuvants and determine adjuvant enhancement, herbicide rates should be used at marginal weed control levels. Effective adjuvants will enhance herbicides at reduced rates and provide consistent results under adverse conditions. However, use of below labeled rates exempts herbicide manufacturers from liability for nonperformance.

Surfactants (nonionic surfactants = NIS) are used at 0.25 to 0.5% v/v (1 to 4 pt/100 gal of spray solution) regardless of spray volume. NIS rate depends on the amount of active ingredient in the formulation, plant species and herbicides used. The main function of a NIS is to increase spray retention, but at a lesser degree, may function in herbicide absorption. When a range of surfactant rates is given, the high rate is for use with low herbicide rates, drought stress and tolerant weeds, or when the surfactant contains less than 90% active ingredient. Surfactants vary widely in chemical composition and in their effect on spray retention, deposition, and herbicide absorption.

Silicone surfactants reduce spray droplet surface tension, which allow the liquid to run into leaf stomata (“stomatal flooding”). This entry route into plants is different than adjuvants that aid in absorption through the leaf cuticle. Rapid entry of spray solution into leaf stomata from use of silicone surfactants often does not result in improved weed control. Silicone surfactants are weed and herbicide specific just like other adjuvants.

Oils generally are used at 1% v/v (1 gal/100 gal of spray solution) or at 2 pt/A depending on herbicide and oil. Oil additives increase herbicide absorption and spray retention. Oil adjuvants are petroleum (PO) or methylated vegetable or seed oils (MSO) plus an emulsifier for dispersion in water. The emulsifier, the oil class (petroleum, vegetable, etc.), and the specific type of oil in a class all influence effectiveness of an oil adjuvant. Oil adjuvants enhance POST herbicides more than NIS and are effective with all POST herbicides, except Liberty and Cobra, and will antagonize Roundup. The term crop oil concentrate (COC) is used to designate a petroleum oil concentrate but is misleading because the oil type in COC is petroleum and not a crop vegetable oil.

MSO adjuvants greatly enhance POST herbicides much more than NIS and PO adjuvants. MSO adjuvants are more aggressive in dissolving leaf wax and cuticle resulting in faster and greater herbicide absorption. The greater herbicide enhancement from MSO adjuvants may occur more in low humidity/low rainfall environments where weeds develop a thicker cuticle. MSO adjuvants cost 2 to 3 times more than NIS and PO adjuvants. The added cost of MSO and increased risk of crop injury when used at high temperatures have deterred people from using this class of adjuvants. Using reduced herbicide rates with MSO adjuvants can enhance weed control while lowering risk of crop injury.

Some herbicide labels restrict use of oil adjuvants and recommend only NIS alone or combined with nitrogen based fertilizer solutions. Follow label directions for adjuvant selection. Where labels allow use of oil additives, PO or MSO adjuvants may be used.

NDSU research has shown wide difference in adjuvant enhancement of herbicides. However, in many studies, no or small differences occur depending on environmental conditions at application, growing conditions of weeds, rate of herbicide used, and size of weeds. For example, under warm, humid conditions with actively growing weeds, NIS + nitrogen fertilizer may enhance weed control to the same level as oil adjuvants. The following are conditions where MSO type additives may give greater weed control than other adjuvant types:

1. Low humidity, hot weather, lack of rain, and drought-stressed weeds or weeds not actively growing due to some stress condition.
2. Weeds larger than recommended on the label.
3. Herbicides used at reduced rates.
4. Target weeds that are somewhat tolerant to the herbicide. (buckwheat, lambsquarters, ragweed to Pursuit or Raptor, or yellow foxtail to Accent).
5. When university data supports reduced herbicide rates. Most herbicides, except Roundup, give greater weed control when used with MSO type adjuvants.

Oil adjuvant applied on a volume or area basis

Labels of many POST herbicides recommend oil adjuvants at 1% v/v. At water volume of 15 or 20 gallons per acre (GPA), 1% oil adjuvant will provide a minimum adjuvant concentration (1% v/v PO in 17 gpa = 1.4 pt/A). The optimum rate of a PO is 2 pt/A. State surveys show common spray volumes are 10 gpa or lower. PO at 1% v/v in 8.5 gpa = 0.68 pt/A and does not provide an sufficient amount of oil adjuvant. Further, in aerial applications at 5 GPA, PO at 1% v/v will not provide sufficient adjuvant. For example, Pursuit and Raptor labels require oil adjuvants to be added at 1.25% v/v or 1.25 gal/100 gal water for aerial application at 5 GPA.

Some herbicide labels contain information on adjuvant rates for different spray volumes. To insure sufficient adjuvant concentration, add oil adjuvant at 1% v/v but no less than 1.25 pt/A at all spray volumes. Surfactant at 0.25 to 1% v/v water is sufficient across all water volumes.

High surfactant oil concentrates (HSOC) were developed to enhance lipophilic herbicides without antagonizing glyphosate. HSOC adjuvants contain at least 50% w/w oil plus 25 to 50% w/w surfactant, are PO or MSO based, and are usually applied at ½ the oil adjuvant rate (area basis). Glyphosate must be applied with other herbicides to control glyphosate tolerant weeds and crops and to delay resistant weeds. Glyphosate is highly hydrophilic, is enhanced by NIS and nitrogen fertilizer surfactant type adjuvants, and is antagonized by oil adjuvants. Postemergence herbicides preferred by growers to mix with glyphosate to increase weed control are lipophilic (Select, Banvel, Laudis, others) and require oil adjuvants for optimum herbicide enhancement. Surfactants are less effective in enhancing lipophilic herbicides. Oil adjuvants, including PO and MSO adjuvants, may antagonize glyphosate. NDSU research has shown wide variability among PO based HSOC adjuvants with many performing no different than common PO adjuvants. However, MSO based HSOC adjuvants enhance both glyphosate and the lipophilic herbicide. MSO based HSOC adjuvants can enhance lipophilic herbicides more than PO based HSOC, MSO and PO adjuvants.

Some water pH modifiers are used to lower (acidify) spray solution pH because many insecticides and some fungicides degrade under high water pH. Most solutions are not high or low enough in pH for important herbicide breakdown in the spray tank. A theory has long been postulated that acidifying the spray solution results in greater absorption of weak-acid-type herbicides. pH-reducing adjuvants (water conditioners/AMS replacment) were developed under this belief. However, low pH is not essential to optimize herbicide absorption.

Many herbicides are formulated as various salts, which are absorbed as readily as the acid. Salts in the spray water may antagonize formulated salt herbicides. In theory, acid conditions would convert the herbicide to an acid and overcome salt antagonism. However, herbicides in the acid form are less water soluble than in salt form. An acid herbicide with pH modifiers may precipitate and plug nozzles when solubility is exceeded, such as with high herbicide rates in low water volumes. Antagonism of herbicide efficacy by spray solution salts can be overcome without lowering pH by adding AMS or, for some herbicides, 28% UAN.

Acidic AMS replacement (AAR) adjuvants contain adjuvants including monocarbamide dihydrogensulfate (urea and sulfuric acid) and some adjuvants in this class are similar to NIS + AMS in enhancing glyphosate and other weak-acid herbicides. The sulfuric acid forms sulfate when reacting with water and can prevent herbicide antagonism with salts in water. The conversion of urea to ammonium is slow but the ammonium formed can partially enhance herbicides. AAR adjuvants must be applied at 1% v/v or greater to achieve the same level of herbicide enhancement as AMS.

Basic pH blend adjuvants are blends of nonionic surfactant, fertilizer, and basic pH enhancer and are used at 1% v/v regardless of spray volume. Data indicate basic blend adjuvants at 1% v/v from 5 to 20 GPA will provide adequate adjuvant enhancement for similar weed control.

Basic pH blend adjuvants are surfactant based, increase spray solution pH, and contain nitrogen fertilizer to enhance herbicide activity. They contain a surfactant to aid in spray retention, spray deposition, and herbicide absorption, and a buffer to increase water pH. Basic pH blends adjuvants increase water pH to near pH 9 which increases water solubility of some herbicides and can increase herbicide phytotoxicity. Within the sulfonyleurea chemistry the magnitude of solubility from high spray solution pH can increase from 40 fold (Harmony GT) to 3,670 fold (UpBeet). The solubility of herbicides in other chemical families increase with high pH: Achieve (1-Dim), florasulam (2-TPS), Everest (2-SACT), Sharpen (14), and diflufenzopyr (19), Callisto and Laudis (27-triketone), and pyrasulfatole and Impact (27-pyrazolone) (numbers represent herbicide mode of action).

Some herbicides degrade rapidly in high pH spray solution. Cobra (diphenylether), Resource and Valor (N-phenylphthalimide), and Sharpen (pH 9) degrade within a few minutes in high pH water but are stable for several days at low pH. Optimum use of pH adjusting adjuvants requires some knowledge of herbicide chemistry or experience. Research has shown that basic pH blend adjuvants may enhance weed control similar to MSO adjuvants and can be used in situations where oil adjuvants are restricted.

Commercial adjuvants differ in effectiveness with herbicides. Data from the table below are from experiments conducted at six NDSU R&E Centers in ND from 1992 through 1995 and repeated in 2005 and 2006 comparing commercial adjuvants with Roundup. In 1993-95, Roundup was applied at 1 to 1.5 oz ae/A to 16 grass and broadleaf weed species. In 2005-06 Roundup was applied at 1 to 4 oz ae/A to 26 grass and broadleaf weed species (272 averages). Higher rates were used in western ND because of low activity in low humidity.

Table 1. Commercial adjuvant effect on glyphosate phytotoxicity.

	Rate % v/v	Grass		Broadleaf	
		1993-95	2005-06	1993-95	2005-06
Surfactants					
		----- % control -----			
None	0.5	49	68	31	42
R-11	0.5	74	90	51	66
APSA 80	0.5	74	87	50	62
Wet-Sol 99	0.5	--	86	--	61
Premier 90	0.5	--	81	--	58
Purity 100	0.5	--	82	--	56
Preference	0.5	67	79	38	58
Liberate	0.5	--	76	--	51
X-77	0.5	66	70	40	52
Spray Booster S	0.5	64	--	41	--
Activator 90	0.5	64	69	41	50
LI-700	0.5	58	66	42	41
Silwet L-77	0.25	56	--	40	--
AMS	8.5 lb/100 gal	--	86	--	68
Surfactant + AMS Fertilizer					
Class Act	2/2.5	90	94	75	76
R-11 + AMS	0.5+8.5 lb/100	--	93	--	76
R-11 + Bronc Max	0.5 + 0.5	--	92	--	73
Surfate	1	89	93	75	74
Dispatch	2	85	--	69	--
R-11 + Cayuse	0.5 + 0.5	82	--	66	--
AMS Replacement / Water Conditioning Agent					
N-Tense	0.5	--	90	--	67
Alliance+Preference	1.25 + 0.5	--	89	--	68
Citron + Preference	2.2 lb/A + 0.5	--	84	--	66
Quest + Preference	0.5 + 0.5	--	83	--	62
Choice + Liberate	0.5 + 0.5	--	81	--	60
Herbolyte		--	79	--	55

Conclusions from the study

1. Not all adjuvants are created equal.
2. Small numerical differences in data is significant as data was averaged across 68 means making outlying values have less affect to change the mean.
3. Most adjuvants enhanced Roundup but some did not enhance Roundup more than no adjuvant added.
4. The better adjuvants in 93-95 are the same as 05-06.
5. Data is arranged in numerically descending order showing similar enhancement in both 93-95 data and 05-06 data.
6. Adjuvants are non-regulated. Changes in individual adjuvant formulations have probably occurred since 1995. However, this data shows relatively little change in herbicides enhancement of Roundup* over time.
7. The 05-06 data is approximately 15 to 20 points higher probably due to higher Roundup* rates used in 05-06.
8. Surfactant + AMS fertilizer adjuvants as a group were more effective than the surfactants or AMS Replacment / Water Conditioning Agent adjuvants.
9. The results are averaged over various locations and may not represent adjuvant effectiveness for all situations.
10. Adjuvants differ in effectiveness and users should compare several products for their specific conditions or select an effective adjuvant from the list.

Spray carrier water quality

Minerals, clay, and organic matter in spray carrier water can reduce the effectiveness of herbicides. Clay inactivates paraquat, diquat, and glyphosate. Organic matter inactivates herbicides. Hard water cations or micronutrients such calcium, magnesium, manganese, sodium, and iron reduce efficacy of all weak-acid herbicides. Cations antagonize glyphosate efficacy by complexing with glyphosate to form salts (e.g. Glyphosate-Ca) that are not readily absorbed by plants. Antagonistic minerals can inactivate the activity of most POST herbicides, including glyphosate, growth regulators (not esters), ACCase inhibitors, ALS inhibitors, HPPD inhibitors, and Ignite. The antagonism is related to the salt concentration. At low salt levels, loss in weed control may not be noticeable under normal environmental conditions but will occur when weed control is marginal because of drought or partially susceptible weeds. The precise salt concentration in water that causes a visible loss in weed control is difficult to establish because weed control is influenced by other factors.

ND water often contains a combination of sodium, calcium, magnesium, and iron and these cations generally are additive in the antagonism of herbicides. Water in ND, SD, and MT is often high in sodium bicarbonate which does not normally occur in other areas of the U.S. Calcium levels above 150 ppm and sodium bicarbonate levels above 300 ppm in spray water can reduce weed control in all situations. Water with 1600 ppm sodium bicarbonate can occur in ND, but total hardness levels can exceed 2,500 ppm.

Ammonium nitrogen increases effectiveness of most weak-acid herbicides formulated as a salt. Fertilizers should always be used with herbicides unless prohibited by label. Ammonium ions greatly enhance herbicide absorption and phytotoxicity even in the absence of antagonistic salts in the spray carrier. However, enhancement of Roundup* and most other POST herbicides from ammonium is most pronounced when spray water contains large quantities of antagonistic cations. Herbicide enhancement by nitrogen compounds appears in most weed species but is most pronounced in species like volunteer corn and species that accumulate antagonistic salts on or in leaf tissue (lambsquarters, velvetleaf, and sunflower).

AMS enhances phytotoxicity and overcomes salt antagonism for weak-acid herbicides formulated as a salt including glyphosate, growth regulators (not esters), ACCase inhibitors, ALS inhibitors, HPPD inhibitors, and Ignite. The antagonism may be overcome by increasing the glyphosate concentration relative to the cation content or by adding AMS and some water conditioners to the spray solution. Effective water conditioners include EDTA, citric acid, AMS, and some acidic AMS replacements. Of these, AMS has been the most widely adopted. When added to a spray solution, the ammonium (NH_4^+) ion complexes with the glyphosate molecule and reduces glyphosate interaction with the hard_water cations, and the sulfate (SO_4^{2-}) ion complexes with the hard_water cations (e.g. calcium sulfate), causing the salt to precipitate from solution. This combined effect increases absorption and efficacy. Natural

sulfate in water can be disregarded but can reduce antagonism if the sulfate concentration is at least three times the calcium concentration.

Antagonism of Roundup by calcium in a spray solution was overcome by sulfuric but not nitric acid, indicating that the sulfate ion was important, but not the acid hydrogen ion. The importance of the sulfate ion explains the effectiveness of ammonium sulfate, and not 28% UAN, in overcoming calcium antagonism of glyphosate. Other herbicides that become acid at a higher pH than Roundup may realistically benefit from a reduced pH as has been shown for Poast. However, Poast does not require a low pH for efficacy. pH of 4 has overcome sodium antagonism of Poast, but nitrogen fertilizer or AMS also will overcome sodium antagonism of Poast without lowering the pH. The ammonium ion provided by these fertilizers is apparently the important ion.

AMS is recommended at 8.5 to 17 lb/100 gal spray volume (1 to 2%) on most Roundup labels. However, AMS at 4 lb/100 gal (0.5%) is adequate to overcome most salt antagonism but more than 4 lb/100 gal may be required to fully optimize herbicides. AMS at 0.5% has adequately overcome antagonism of glyphosate from 300 ppm calcium. Use at least 1 lb/A of AMS when spray volume is more than 12 gpa. The amount of AMS needed to overcome antagonistic ions can be determined as follows:

$$\text{Lbs AMS/100 gal} = (0.002 \times \text{ppm K}) + (0.005 \times \text{ppm Na}) + (0.009 \times \text{ppm Ca}) + (0.014 \times \text{ppm Mg}) + (0.042 \times \text{ppm Fe})$$

This does not account for antagonistic minerals on or in the leaf tissue in species like lambsquarters, sunflower, and velvetleaf which may require additional AMS.

AMS may contain contaminants that may not dissolve resulting in plugged nozzles. Use spray grade AMS to prevent nozzle plugging. Commercial liquid solutions of AMS are available and contain approximately 3.4 lbs of AMS/gallon. For 8.5 lbs of AMS/100 gallons of water add 2.5 gallons of liquid AMS solution.

28% UAN fertilizer is effective in enhancing weed control and overcoming mineral antagonism of most POST herbicides, but not calcium antagonism of Roundup. Sodium bicarbonate antagonism of Poast is overcome by 28% UAN and AMS. AMS or 28% UAN does not preclude the need for an oil adjuvant with lipophilic herbicides. Generally, 4 gal of 28% UAN/100 gal of spray has been adequate. AMS and 28% UAN enhance herbicide control of most weeds even in water without antagonistic salts. Nitrogen fertilizer/surfactant blends may enhance weed control of most herbicides formulated as a salt.

Analysis of spray water sources can determine water quality effects on herbicide efficacy. Water samples can be tested at the NDSU Soil and Water Laboratory:

USPS: NDSU Dept 7680, Fargo, ND 58108-6050,

UPS and Physical Address: Waldron Hall 202, 1360 Bolley Dr. NDSU, Fargo, ND 58102. (701) 231-7864.

Analysis is approximately \$25.00 to \$29.00.

The analysis may report salt levels in ppm or grains. To convert from grains to ppm, multiply by 17 (Example: 10 grains calcium \times 17 = 170 ppm calcium). AMS at 2% (17 lb/100 gallons water) will overcome antagonism from the highest calcium and/or sodium concentrations in North Dakota water. However, AMS at 4 lb/100 gal is adequate for most North Dakota water. Iron is also antagonistic to many herbicides but not abundant in ND water.

Water conditioner adjuvants are liquid for user preference, applied at low use rates, may contain no or very little AMS, may lower spray solution, and are advertised to replace AMS, and thus are also called AMS replacement adjuvants. Pesticide applicators prefer the convenience of low use rate water conditioners, but performance has been inconsistent. Glyphosate plus commercial water conditioner products that included AMS at the equivalent rate of 1% w/w can give similar control to 1% w/w (8.5 lbs/100 gal) AMS. Commercial water conditioners that do not provide an equivalent amount of AMS give less control than glyphosate with 1% or 2% w/w AMS and are often no better than glyphosate alone.

Acidic AMS replacement (AAR) adjuvants have been developed for use with glyphosate and other weak acid herbicides. Claims have been made to enhance herbicide activity, and negate the effects of antagonistic salts in spray water and the antagonism from micronutrient solutions added for crop health. Most adjuvants in this class contain monocarbamide dihydrogen sulfate or AMADS (urea plus sulfuric acid) which lowers spray solution pH to 1.4 to 3. The low pH is below the pKa of postemergence herbicides causing most herbicide molecules to be in the acid state which results in fewer molecules binding to positively charged salts.

Some water conditioner adjuvants and acidic AMS replacement adjuvants (AAR) are marketed to modify spray water pH, but low pH is not required for herbicide efficacy. The type of acid or components of buffering agents and the specific herbicide all need to be considered before using pH-modifying agents. Several commercial AAR adjuvants applied with glyphosate in distilled water were tested and ranked as follows: surfactant + AMS > AMS > NIS = AAR. A commercial AAR adjuvant composed primarily of sulfuric acid was much less phytotoxic than most AAR adjuvants which support the concept and use of ammonia to enhance weak acid herbicides. Generally, AAR adjuvants applied with glyphosate in 1000 ppm hard water (Ca and Mg) gave similar weed control as when applied in distilled water supporting the theory of non-binding herbicide molecules when pH is below the pKa of the herbicide. Clearly, commercial adjuvants vary greatly in function, use, and chemical and biological effect.

Low spray volumes (5 to 10 gpa) have been equally or more effective than higher spray volumes for many herbicides. Low spray volume originally was considered important to glyphosate efficacy because it would reduce the ratio of glyphosate and antagonistic cations in the spray solution. However, low spray volumes have enhanced glyphosate efficacy because of higher glyphosate concentration in the spray deposit. Greater efficacy from higher concentrated droplets has been shown with many other herbicides but is logical that the highly concentrated droplets with low volume would be positive for translocated herbicides (NDSU Pile Theory). Contact herbicides (Cobra, Cadet, Ignite, Flexstar/Reflex, paraquat, Sharpen) require higher spray volume for adequate and thorough coverage to enhance control.

Low spray volumes usually imply use of low-volume nozzles that produce small droplets which can increase off-target movement. However, drift-reducing nozzles have been developed that produce large droplets at low volume. In low spray volumes, larger droplets produced by drift-reducing nozzles have been equally effective as small droplets with several translocating herbicides. However, coarse or larger droplets may be less phytotoxic than fine and medium size droplets for sethoxydim, imazethapyr, tembotrione, and 2,4-D. Limited research is available about efficacy based on droplet size although will become important as regulation requires larger droplet size to mitigate drift from small droplets.