Spray Water Quality Issues for the Turf Manager: Dealing with pH and Hardness

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Have you ever applied an herbicide only to see some weed species continue to grow in the turf? Perhaps the insecticide application did little to decrease the spread of the insect pest across the golf course. Usually, we attribute that lack of activity on such things as lack of equipment calibration, the wrong timing of the application, or poor product selection when the application fails to control the pest.

Seldom is the water used to mix and apply the product considered as a potential factor in a less than successful pesticide application. Are you aware of reports that half of some pesticides can break down in the spray tank in less than one hour in alkaline spray water? Did you realize that the commonly used herbicide, glyphosate, can be rendered less effective when the spray water contains high levels of calcium, iron, and magnesium? What this says is that it is important to understand the quality of the water being used to mix pesticides in order to achieve consistent results from application to application.

This publication provides turf managers guidance on enhancing the efficacy of pesticides added to the spray tank by examining how water might influence the performance of those products. A discussion is provided on common water quality factors that affect efficacy, how to measure water quality parameters (i.e. pH and hardness), what to look for in pesticide labels regarding directions to improve water quality, and how to correct water quality issues when they are problematic so that you can maximize the effectiveness of your products and your financial investment.

Two other publications provide additional information on water quality issues and the use of adjuvants to improve product efficacy.

• The Impact of Water Quality on Pesticide Performance (Purdue Extension publication PPP-85, available from the Purdue Extension Education Store: www.the-education-store.com)

• Understanding Adjuvants and the Water Droplet: Improving the Dose-Transfer from the Tank to the Target Pest (Purdue Extension publication PPP-106, available from the Purdue Extension Education Store: www.the-education-store.com)

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Potential hydrogen (pH) measures the acidity or alkalinity level of the spray solution. A pH reading of <7 means the solution is acid, pH = 7 is neutral; and a pH > 7 is alkaline. The pH of spray water directly influences how quickly the chemical degrades in spray tank (measured as half-life), how much of the pesticide goes into solution (solubility), and the degree of which the pesticide breaks apart (dissociation). Most spray water derived from groundwater (wells) or surface water (rivers, lakes, ponds) has a pH ranging from 7.5 to 9.0 meaning it is an alkaline solution.

Using spray water with a pH greater than 7 (alkaline) could lead to soluble pesticides breaking down in the tank. The longer it takes from adding the product to making the application, the more likely you are

going to have a problem. This is particularly true of older pesticides. In all cases, spraying immediately after mixing reduces the likelihood of problems.

It is important to mention that not all pesticide products break down in alkaline water. In fact, most products are not strongly influence by spray tank water pH. Usually, a high spray water pH is bad but some herbicides in a class known as sulfonylureas actually prefer mixing in alkaline water.

There are a number of ways to measure the pH of water, including sending a sample to a laboratory for analysis. A portable pH meter can be another option. The most economic option is to use test strips that are used to test the pH of pools, spas, and aquarium water which normally cost \$7-18 for a kit with 50 test strips. By the test strip kit that tests for both pH and hardness.

The majority of turf pesticides are stable in waters with a pH of under 8, but some like trichlofon (Dylox 420 SL), carfentrazone (Quicksilver) and iprodione (26GT) are among products prone to breaking down (through a process called alkaline hydrolysis) quickly in high pH water (pH > 8), preferring to be mixed and spayed in pH of less than 7). These and other similar products have half-lives of only a few hours or minutes when your spray pH is \geq 9.0, which can reduce the efficacy of the products. The more soluble the ingredient, the more likely that alkaline hydrolysis can break down the pesticide.

Weak acid herbicides like 2,4-D and glyphosate dissociate when spray water pH is higher than the herbicide's pKa (acid dissociation constant) and are less likely to be absorbed by weed foliage and more likely to be antagonized by cations (calcium, magnesium and others) present in the water. These weak acid herbicides prefer being applied in spray water with a lower pH of 4-6 but they usually work well at a high range of spray water pH (Table 1).

However, some pesticides prefer being mixed in a higher pH spray water. For instance, the label for Junction fungicide which is a combination of copper hydroxide + mancozeb warns that phytotoxicity (plant burn) may occur on turf when the product is mixed in spray water with a pH <6.5. Other labels like Monument 75WG (trifloxysulfuron) and Revolver (foramsulfuron) encourage using spray water near pH=7.0. Tables 1-4 provide information on water quality parameters from the product label or other published sources.

Getting the correct pH for the product(s) intended to be added to the tank is rather easy. First, look at the tables to know what pH your product prefers. Always refer back to the product label to find the current label directions. If no information is available in the label, then likely the product will work at a wide pH range.

Second, know if the product you are using might already be formulated with a buffering agent in the jug. Products such as Signature XTRA Stressguard, Proxy (ethephon) and glyphosate (Roundup) often contain buffering agents to acidfy the spray tank water and no additional buffering agent is needed. Lastly, if your pH is too high or too low for the product you are mixing, you can first add a buffering agent to adjust the pH of your spray water. Buffering agents are one class of adjuvant. Some buffering agents raise pH but most lower pH so make sure to pick the right one. These buffering agents will help to hold your spray water pH in the desirable range once added to the tank. Some labels like Octane (pyraflufen), Certainty (sulfusulfuron), Scimitar GC (lambda-cyhalothrin) and others provide specific notes on the ideal pH range to achieve with the buffer. You can use a jar test to verify compatibility.

Water Hardness

Water hardness is a measure of the total concentration of positively charged minerals (cations) in water. Calcium (Ca²⁺), magnesium (Mg²⁺), and iron (Fe^{2+, 3+}) are cations which in sufficient quantities can make water hard. Water hardness is always reported as calcium carbonate (CaCO₃) equivalents and typically as ppm (mg/L). The US EPA defines soft water as <75 ppm, moderately hard water as 75-150 ppm, hard water as 150-300 ppm, and very hard water as >300 ppm. Hard water is found in water derived from wells, rivers, or city/municipality sources. Conversely, rain water collected is considered soft as the water has no dissolved the minerals from the soil. An important fact to remember is that water pH and water hardness are independent of one another. That is why it is important to test both the pH and hardness of the water that will be used to mix the pesticides.

Much like pH, water hardness can be measured with a drinking water test kit. Water hardness tests report the hardness of the water in grains per gallon or in ppm. It is easy to convert grains into ppm in that 1 grain per gallon = 17.1 ppm. The most economic option is to use test strips as previously described in the section on pH. Find test strips that test hardness from 0 up to 400 ppm or more.

Why and when is hardness a problem with commonly used turf pesticides? Water hardness can be a problem when a weak acid herbicide is used (Table 1), but hardness is not known to cause problems with the fungicides, insecticides, and plant growth regulators used on turf. Water hardness causes problems with the amine and choline formulations of weak acid herbicides when the cations bind to the herbicides, reducing their effectiveness. Ester formulations are not antagonized. Glyphosate is the best example of a weak acid herbicide that is antagonized by hard water, but water hardness is known to antagonize (work against) other weak acid herbicides like 2,4-D amine, bentazon, dicamba, glufosinate, MCPA, quinclorac, and sethoxydim,.

The good news is hard water antagonism to weak acid herbicides is overcome by adding dry ammonium sulfate $(AMS) [(NH_4)_2SO_4]$ or its equivalent in liquid form to the spray tank. Dry ammonium sulfate dissolves in water after a short period of agitation in the spray tank. Research has shown that adding 4.25, 8.5 or 17 lbs. AMS/100 gallons spray water (this is 0.5, 1.0, and 2.0% by weight) overcomes antagonism. The harder the water means more AMS is needed. One easy way of determining the amount needed is to follow the product label. Adding 8.5 lbs AMS/100 gallons of spray water is sufficient to overcome hard water antagonism in most hard water sources.

AMS may reduce water pH by about one-half a unit (like from 7.5 to 7.0), but this slight reduction of pH is not why AMS is used. It is important to note that AMS does not remove the cations such as calcium and magnesium from the water. Instead AMS sequesters (binds) those minerals to allow the herbicide to remain unattached in water.

How exactly does AMS work? The sulfate, (SO4⁻²,) in ammonium sulfate binds to Ca^{+2} and the NH_4^+ binds to the negatively-charged weak acid herbicide. An alternate to AMS are liquid "water conditioning"

agents sold under many trade names. These conditioners usually contain ammoniated ions and these liquid products are also effective at reducing problems with hard water.

Other Things to Consider

Aside from water pH and hardness, you should consider the following water quality parameters that may impact pesticide efficacy in some circumstances.

Alkalinity is a measure of the acid-neutralizing or buffering capacity of water. Alkalinity measures carbonate ($"CO_3^{-2"}$), bicarbonate (HCO^{3-}) and hydroxyl (OH^{-}) anions. Alkalinity is reported as CaCO₃ equivalents. Alkalinity becomes a problem to some herbicides when levels exceed 300 to 500 ppm. The herbicides 2,4-D amine, MCPA amine, and the "-dims" (clethodim, sethoxydim, etc.). Alkalinity is not thought to be as problematic as water pH and hardness but it is also a less researched topic.

Turbidity is a measure of suspended organic solids in the spray water solution. Turbidity becomes a problem when the water is cloudy, murky, discolored, or muddy. Turbidity causes a problem with a relatively few herbicides that tightly bind to soil particles. Examples include glyphosate, paraquat, and others. Labels provide warnings about using high turbidity water. The solution is to find an alternate water source.

Fertilizer and herbicide tank-mixes can sometimes be antagonistic in the tank. FeSO₄ (iron sulfate) is known to antagonize products like 2,4-D, MSMA, glyphosate, imazamox, and mefluidide. Other micronutrients like Zinc (Zn) and Manganese (Mn) are known to sometimes cause antagonism when tank mixed with weak acid herbicides, so use caution when tank-mixing micronutrient fertilizers, liquid calcium, and Epsom salts with herbicides.

Use caution when spraying with water high in *salinity*. Salinity is a measure of salts in the water. Herbicides like atrazine, MCPA, and simazine can be antagonized by saline water, while other herbicides can safely be used in saline water. Much is unknown about the influence of saline water on pesticide efficacy so avoid using these water sources when possible.

Importance of Reading Product Labels

Your best move is to always read the label of the pesticides being used. Some will provide clear instructions to alter the pH or the hardness or both. When these instructions are provided by the manufacturer, it is important to follow their advice if you expect to maximize the performance of the product.

There are numerous instances where the label does not address pH or hardness. While the label is silent on the subject, there may be benefits from adjusting either or both the pH and hardness. Check with the sales representative of the product or the dealer serving the product to see if they have any data or experiences to suggest that using an adjuvant in altering the pH and water hardness can improve the performance of the product in your area.

Conclusion

The constituents of water and whether or not it's acid or alkaline can influence how well a product works. Dealing with these aspects of your spray program is actually not much different than any other technical aspect of turf management. Today's turf managers are fine-tuning all aspects of their turf program. Which turfgrass cultivars to plant, the quality of the sand put in the bunkers, soil-moisture sensors for irrigation management, and other practices continued to be refined as the science of turf management continuously evolves from yesterday to today.

It is for these vary reasons that the spray application process be improved to continue to push for better controls of insects, weeds, and diseases. The pursuit is no longer just 90% control, but as close to 100% as possible. Whether it's choosing the right product, timing of application, or the selection of better nozzles, all can lead to more precise applications. This is why it is important to look at the quality of water, because in some cases, it might be the one factor that prevents the products from providing superior performance.

A few points to remember include the following:

- Water can negatively impact pesticide performance.
- Water pH and hardness can cause problems with some pesticides.
- We know that labels can warn us about pH and hardness, but many are silent on water quality.
- We know that cutting rates or low-use rate products requires better water.
- We know checking pH and hardness of water, regardless of its source, is worth the time and money spent on the tests considering it only represents pennies on the dollars spent on the application to turf.
- The ideal spray tank water pH varies by product, and can be adjusted higher or lower using the correct buffering or acidifying agents.
- Water hardness should be low (<150 ppm) when spraying glyphosate and <400 when spraying other weak acid herbicides (see those shaded red in Table 1).
- Hard water can be corrected by using water conditioning agents such as ammonium sulfate.
- Adjuvants that fix the pH and water hardness can cost \$0.60 to \$2.00 per acre.
- A small amount of effort on your part to test spray water when combined with knowledge of the pesticides and labels will ensure that the products are providing the highest level of weed, insect, and disease control.

Water pH Response Key		Water Hardness Response Key			
This product will be effective at this water pH.	This product may be subject to alkaline hydrolysis at this pH, label statements suggest that this pH is not	This product is subject to alkaline hydrolysis at this pH or label statements suggest that this pH is not	Water hardness is not a concern with this product.	Water hardness may be a concern since this is a weak acid herbicide. More research is needed.	Water hardness is a concern. Add ammonium sulfate or another water conditioning agent to prevent hard
	ideal, or research suggests that this pH may not be ideal because of its chemistry.	ideal. Use a buffering agent to correct the water pH before mixing.			water antagonism.

Table 1. Effect of Spray Water pH and Hardness on Turf Herbicides.

Herbicide	Trade Name	Acidic	Neutral	Alkaline	Water
		Spray	Spray	Spray	Hardness
		Water	Water	Water	
		(pH 4-6)	(pH 7)	(pH 8-9)	
2,4-D amine	2,4-D Amine 4, Saber, Weedar 64, others				
2,4-D ester	Barrage HF, Shreddar, Weedone LV4 EC				
atrazine	AAtrex 4L, AAtrex Nine-O, Atrazine 4L, Atrazine				
	90DF				
amicarbazone	Xonerate 70 WDG				
asulam	Asulox				
benefin					
bensulide	Bensumec 4FL				
bentazon	Basagran T/O, LescoGran				
bispyribac-sodium	Velocity SG				
bromoxynil	Broclean, Buctril, Buctril 4EC, MOXY 2E				
carfentrazone	QuickSilver, QuickSilver T & O				
chlorsulfuron	Chlorsulfuron 75, Corsair, Telar XP				
clopyralid	Lontrel				
dazomet	Basamid				
DCPA	Dacthal				
dicamba	Banvel, Diablo, Vanquish				
diclofop	Illoxan				
dimethenamid	Tower				
diquat	Diquat SPC 2 L, RedWing, Reward, others				
dithiopyr	Dimension, Dithiopyr, others				
ethofumesate	Prograss, Prograss SC				
fenoxaprop	Acclaim Extra				
flazasulfuron	Katana				
florasulam	Defendor SC				
fluazifop	Fusilade II, Ornamec				
flumioxazin	SureGuard				
fluroxypyr	Vista				

Herbicide	Trade Name	Acidic	Neutral	Alkaline	Water
		Spray	Spray	Spray	Hardness
		Water	Water	Water	
		(pH 4-6)	(pH 7)	(pH 8-9)	
foramsulfuron	Revolver				
glufosinate	Finale				
glyphosate	Departure, Glyphosate T&O, Roundup, others				
halosulfuron	Halosulfuron Pro, SedgeHammer, others				
imazaquin	Image				
imazapic	Plateau				
imazosulfuron	Celero				
indaziflam	Specticle FLO				
isoxaben	Gallery, Isoxaben 75WG				
MCPA amine	MCPA-4 Amine				
MCPA ester	MCPA ester 4				
mecoprop (MCPP)	MCPP-p 4 Amine, Mecomec 2.5, Mecomec 4				
mesotrione	Tenacity				
metolachlor	Pennant MAGNUM				
metribuzin	Sencor 75%				
metsulfuron	Manor, Mansion, MSM Turf				
MSMA	MSMA 6.6, MSMA 6 Plus, TARGET, others				
oryzalin	Oryzalin, Proazlin 4L, Surflan, others				
oxadiazon	Ronstar 50WSP, Ronstar Flo, Oxadiazon, others				
pendimethalin	Pendulum 3.3EC, Pendulum Aqua Cap, others				
penoxsulam	Sapphire, Lockup				
prodiamine	Barricade. Prodiamine, others				
pronamide	Kerb 50WP				
pyraflufen ethyl	Octane 2% SC				
quinclorac	Drive XLR8, Quinclorac, others				
rimsulfuron	Quali-Rimsulfuron 25DF, TranXit				
sethoxydim	Sethoxydim E Pro				
siduron	Tupersan, Tupersan 470, Crabgrass Control				
simazine	Princep, Simazine 4L, Simazine 90DF, others				
sulfentrazone	Dismiss, Spartan 4F				
sulfosulfuron	Certainty				
topramezone	Pylex				
Triclopyr amine	Triclopyr 3 AMINE				
Triclopyr ester	Turflon Ester, Turflon Ester Ultra, Triclopyr 4				
trifloxysulfuron	Monument 75WG				
trifluralin	Treflan				

Fungicide	Trade Name	Acidic Spray	Neutral Spray	Alkaline Spray	Water Hardness
		(pH 4-6)	(pH 7)	(pH 8-9)	
acibenzolar-S-methyl	Plant activator in Daconil Action premix	(p11 + 0)	(0117)	(p:10.5)	
azoxystrobin	Heritage 50 WG, Heritage G, Heritage TL				
boscalid	Emerald				
captan	Captan				
chloroneb	Teremec SP				
chlorothalonil	Chlorothalonil, Daconil, others				
Copper hydroxide +	Junction				
mancozeb					
cyazofamid	Segway				
difenoconazole	Briskway premix				
etridiazole	Terrazole 35 WP				
fluazinam	Secure				
fluidoxonil	Medallion 50 WP				
fluoxastrobin	Disarm 480 SC				
flutolanil	ProStar 70 WP				
fluxapyroxad	Xzemplar				
fosetyl-Al	Chipco Signature, Fosetyl-AL 80 WDG				
iprodione	26 GT, Chipco 26019, Ipro 2SE				
mancozeb	Fore 80 WP				
mefenoxam	Mefenoxam 2 AQ, Subdue GR, Subdue Maxx				
metconazole	Tourney				
mineral oil + pigment	Civitas				
mycobutanil	Eagle 20 EW, Myclobutanil 20 EW T&O				
PCNB	Turfcide				
penthiopyrad	Velista				
phosphite	Alude, Appear				
polyoxin D	Affirm, Endorse 2.5 WP				
propamocarb	Banol				
propiconazole	Banner Maxx gal, Propiconazole 14.3				
pyraclostrobin	Insignia 20 WG				
tebuconazole	Torque				
thiophanate-methyl	ArmorTech TM, Cleary's 3336				
triademefon	Bayleton 50 T&O, Bayleton FLO				
trifloxystrobin	Compass 50 WDG				
triticonazole	Trinity, Triton FLO				
vinclozolin	Curalan EG				

Table 2. Effect of Spray Water pH and Hardness on turf fungicides.

Insecticide	Trade Name	Acidic Spray Water (pH 4-6)	Neutral Spray Water (pH 7)	Alkaline Spray Water (pH 8-9)	Water Hardness
acephate	Orthene 75 WSP				
Baccillus thuringiensis kurstaki	Dipel Pro DF				
bifenthrin	Talstar GC				
cabaryl	Sevin SL				
chlorantranili-prole	Acelepryn 0.2 G, Acelepryn 1.67 SC, Provaunt				
chlorpyrifos	Chlorpyrifos 4E, Dursban 50WSP				
clothianidin	Arena 50 WDG, Arena 0.25 G				
cyfluthrin	Tempo Ultra GC SC125, Tempo Ultra SC Ultra				
deltamethrin	DeltaGard T&O 5 SC				
dinitrofuran	Zylam L				
fipronil	TopChoice				
hydramethylnon	Amdro				
imidacloprid	Imidacloprid ArmorTech, Merit 0.5G, Merit 75 WSP, Merit 2F				
indoxacarb	Advion				
lambda-cyhalothrin	Scimitar GC				
spinosad	Conserve SC				
thiamethoxam	Meridian 0.33G, Meridian 25 WG				
trichlorfon	Dylox 420 SL, Dylox 6.2 G				

Table 3. Effect of Spray Water pH and Hardness on turf insecticides.

Table 4. Effect of Spray Water pH and Hardness on turf plant growth regulators.

Plant Growth Regulator	Trade Name	Acidic Spray Water (pH 4-6)	Neutral Spray Water (pH 7)	Alkaline Spray Water (pH 8-9)	Water Hardness
ethephon	Ethephon 2, Ethephon 2SL, Proxy				
flurprimidol	Cutless 50W, Cutless MEC				
gibberellic acid	ProGibb T&O				
mefluidide	Embark, Embark 2-S				
trinexapac-ethyl	Primo Maxx, Trinexapac-Ethyl, others				