# HOW SOIL PH AFFECTS THE ACTIVITY AND PERSISTENCE OF HERBICIDES

**Soil Acidification Series**

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# How Soil pH Affects the Activity and Persistence of Herbicides

## Abstract

Decreasing soil pH, also called soil acidification, is a growing concern in eastern Washington and northern Idaho. Researchers and farmers have measured soil pH values below 5.0 throughout the Palouse region, in particular. Decreasing soil pH has serious implications for the cropping systems of the Palouse.

This publication, *How Soil pH Affects the Activity and Persistence of Herbicides*, discusses how decreasing soil pH contributes to increased instances of herbicide persistence. The publication categorizes commonly used herbicides as either a weak acid, weak base, cationic, nonionic polar, or nonpolar and briefly explains how the soil/herbicide interactions within each category can be affected by pH.

The Soil Acidification series begins with *An Introduction*, covering the fundamentals of soil pH and acidification, and continues with other fact sheets on more specific topics such as the influence of pH on pathogens and microbes, recommended varieties of specific crops, crop nutrition, and liming.

## Introduction

Instances of herbicide persistence contributing to crop injury in the dryland regions (DLR) of the inland Pacific Northwest (PNW; eastern Washington, northern Idaho, and northeastern Oregon) are common. A major concern related to cases of herbicide persistence is the soil *pH* in the region.

Soil pH can have substantial effects on the activity and persistence of herbicides in soil, particularly at pH extremes of 4.5 or below and 7.5 or above (Monaco et al. 2002). Therefore, there is a need to understand how the pH of soils in the inland PNW-DLR will influence the persistence of herbicides commonly applied. A knowledge and understanding of the chemical and physical properties associated with herbicides is needed in order to understand how soil pH influences persistence.

The most common way herbicides are grouped is by their site of action. Both the Weed Science Society of America (WSSA) and the Herbicide Resistance Action Committee (HRAC) have systems for classifying herbicides according to their site of action. For example, the active ingredient of PowerFlex HL is pyroxsulam, an inhibitor of acetolactate synthase (also known as acetohydroxy acid synthase) in plants, and is classified by the WSSA as a Group 2 (HRAC classification: B) herbicide.

***Important Soil/Herbicide Interaction Terms:***

**adsorption**. The association or binding of molecules with the surfaces of solids.

**anion**. An ion or molecule that has a net negative charge.

**cation**. An ion or molecule that has a net positive charge.

**half-life.** The time required for half of applied molecules to be degraded.

**ion.** An atom or molecule that has acquired a net electric charge by gaining or losing one or more electrons.

**ionization.** The process by which a molecule acquires a negative or positive charge by gaining or losing electrons to form ions.

**pH**. A measure of the concentration of hydrogen ions in a system, known as the master variable.

**weak acid.** An acid that dissociates (loses a hydrogen ion) only slightly in water to produce an acid solution.

**weak base.** A molecule that associates with hydrogen ions only slightly in water to produce an alkaline solution.

Classifying herbicides by mechanism of action is convenient for recalling trends in weed control and crop selectivity, as well as for designing herbicide rotation programs to avoid selection of herbicide resistant weeds. However, when considering herbicide properties and how soil pH could affect herbicide persistence in soil, it is important to classify herbicides based on charge (ionic) and polarity properties.

In chemistry, "*ion*" refers to an atom or molecule that bears a net positive or negative charge—that is, the number of electrons is not equal to the number of protons. Thus, properties of herbicides depend on the change of the herbicide's overall charge from neutral to a net positive or negative charge.

The significance of understanding the charge of a given herbicide in a soil is important because soil colloids (clay and organic matter) are negatively charged (*anions*, or anionic particles).

Therefore, herbicides with a net positive charge (*cations*, or cationic molecules) will be strongly attracted to the negatively charged soil colloids, while negatively charged herbicides (also anions) will be repelled from soil colloids (Ross and Lembi 1999; Monaco et al. 2002).

The *polarity* of a molecule refers to a separation of charge across the molecule. Many chemicals, like water or alcohol, do not bear a net charge, but one side of the molecule has more negative charge, while the other is more positive. Like a magnet, the molecule is "polar."

The charge of an herbicide along with polarity are both important factors determining the water solubility of herbicides. The water solubility of an herbicide is the maximum amount of herbicide that will dissolve in water (Hanson et al. 2004). In the context of herbicide–water interactions, increasing polarity of herbicides will result in increased water solubility, because water is polar and "like dissolves like."

As shown in Figure 1, there are five categories, based on the charge and polarity properties, by which herbicides can be classified (McBride 1994):

- weak acid,
- weak base,
- cationic,
- nonionic polar, and
- nonpolar.

The nonionic polar chemicals can vary from weak to moderate polarity. At a neutral soil pH (7.0), *weak acid* herbicides will be predominantly negatively charged, and at an acid pH, weak acids will be predominantly neutral. *Weak base* herbicides in acid soils will be predominantly positively charged, and in neutral soils, weak bases will be predominantly neutral.

As Figure 1 illustrates, nonionic herbicides will exist without a charge at all soil pH values and cationic herbicides will always exist in a positively charged form (Monaco et al. 2002).

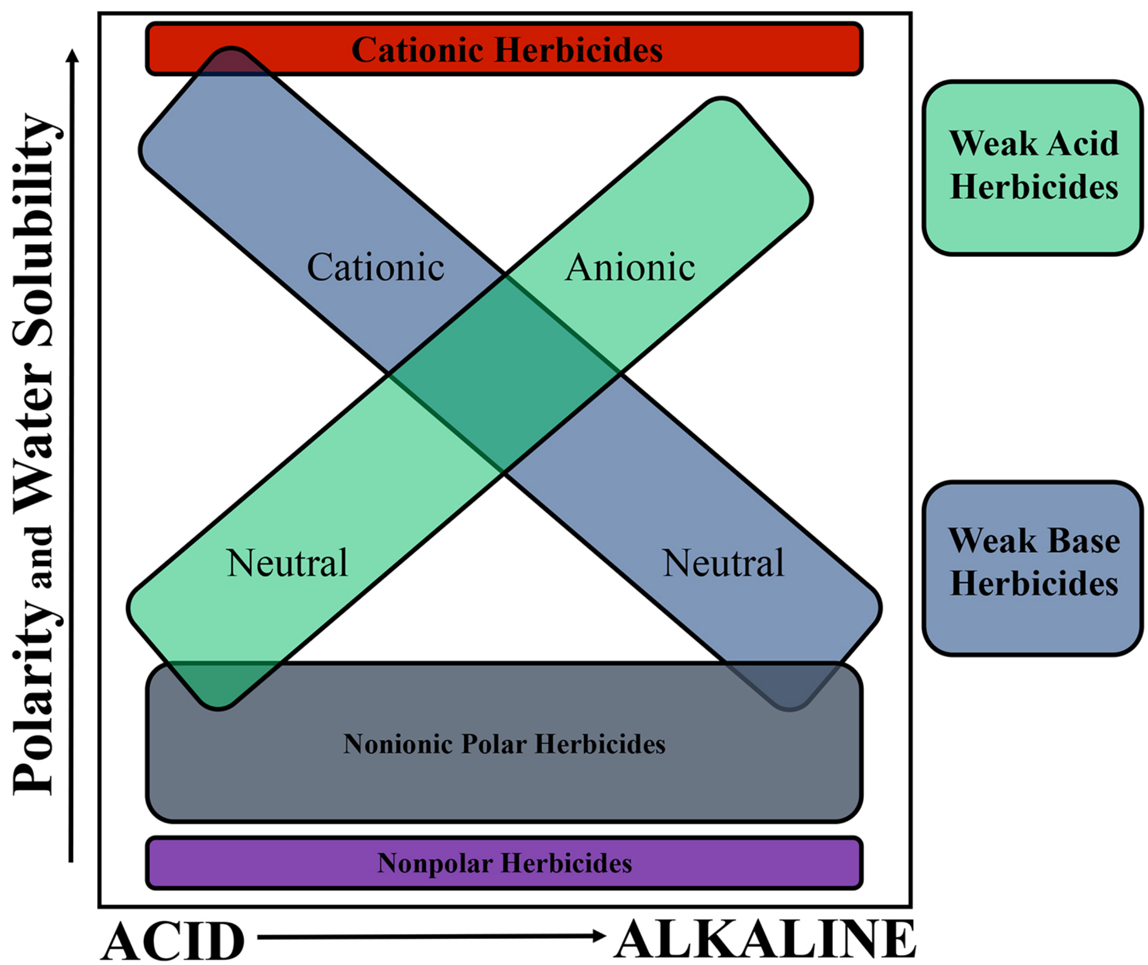


Figure 1. Classification of herbicides based on charge and polarity properties as pH changes from acid to alkaline. Adapted from Environmental Chemistry of Soils (McBride 1994).

## Weak Acid Herbicides

Of the 48 herbicide active ingredients used in the inland PNW-DLR, 33 are classified as weak acids (Table 1). Weak acid active ingredients are found in products such as:

- Assure II (Group 1, A),
- Beyond (Group 2, B),
- Pursuit (Group 2, B),
- GoldSky (Group 2, B and 4, O),
- PowerFlex HL (Group 2, B),
- Everest 2.0 (Group 2, B),
- 2,4-D (Group 4, O),
- WideMatch (Group 4, O),
- Huskie (Group 27, L and 6, $C_3$),
- Roundup PowerMax (Group 9, G), and
- Sharpen (Group 14, E).

The activity and persistence of some herbicides classified as a weak acid will likely not be affected by decreasing soil pH due to a short soil *half-life* or lack of herbicidal activity in the soil, but some weak acid herbicides are known to persist in soil with continued activity. In the latter cases, decreasing soil pH may be a major factor determining persistence if it alters the charge and, therefore, the *adsorption* and water solubility properties of the herbicide.

Of the herbicides that are classified as weak acids, the Group 2 (B) herbicides will persist across a wide soil pH range, and are good examples of the variation in soil activity and persistence that can exist within a single mode of action. While focusing on the imidazolinones (e.g. Beyond and Pursuit), sulfonylureas (e.g. Osprey and Glean XP), and the triazolopyrimidines (e.g. PowerFlex HL), it is important to understand the effects that water solubility can have on the activity and persistence of herbicides.

Most Group 2 herbicides have increasing water solubility as pH increases (e.g. pyroxsulam: 16.4 mg/L at pH 4, 3200 mg/L at pH 7, and 13700 mg/L at pH 9). See Table 2. As pH increases from 4 to 9, the compound becomes more negatively charged. Negatively charged compounds are generally more polar and therefore, more soluble in water than neutral compounds (Figure 1). The soil solution pH, as a result, influences the distribution of herbicides among the water, solid, and gaseous phases of the soil (Hanson et al. 2004). Use Table 1 to find the active ingredients in commonly used products, and then reference Table 2 for the water solubility of the active ingredient.

***Herbicides with relatively short half-lives can carryover and cause injury to crops that are extremely sensitive to small amounts of the herbicide.***

Imidazolinones and triazolopyrimidines are weak acids and will have increased persistence in lower pH soils. Increased persistence at lower soil pH is a result of the change from a net negative charge at higher pH values to a neutral charge at lower pH values (Figure 1). The neutral charge, resulting in decreased water solubility, reduces the repulsion by like charged soil organic matter. Therefore, as the soil pH decreases, both imidazolinones and triazolopyrimidines become more hydrophobic (water-hating), and are more likely to associate with the soil organic matter fraction rather than the water, making the herbicide less active and less available for microbial degradation.

The sulfonylureas are more likely to have increased persistence at higher soil pH, even though the sulfonylureas have generally the same increasing water solubility with increasing pH as the imidazolinones and triazolopyrimidines. The reason that sulfonylureas have increased persistence at higher soil pH, rather than at lower pH like the imidazolinones and triazolopyrimidines, is because sulfonylureas undergo non-microbial degradation at lower soil pH, leading to increased rates of degradation in acid soils. Therefore, persistence of sulfonylureas is not necessarily related to soil, but, rather is, a result of continued herbicidal activity from extremely low concentrations of the herbicide in the soil. Some sulfonylurea herbicides can continue to cause injury to following crops for several half-lives after application (Hanson et al. 2004).

## Nonionic Herbicides (Weakly to Moderately Polar, and Nonpolar)

Thirteen active ingredients used in the inland PNW-DLR are nonionic at both acid and alkaline pH (Figure 1). The active ingredients are found in products such as:

- Lorox (Group 7, $C_2$),
- Valor SX (Group 14, E),
- Axiom (Group 15, $K_3$ and 5, $C_1$), and
- Zidua (15, $K_3$) (Table 1).

Many of the nonionic active ingredients, listed in Table 2, are primarily degraded by soil microorganisms, mostly bacteria and fungi. Some factors that affect the rate at which microorganisms degrade herbicides include soil temperature, moisture, and pH.

Table 1. Common Herbicide Products, Grouped by Charge and Polarity Properties. Common herbicides used in the inland PNW-DLR are grouped by the charge of the active ingredient and polarity classification, and presented in alphabetical order within each classification. The products that contain active ingredients where the water solubility changes with pH are bolded and underlined.

| Trade name; Active ingredients in product | |
|---|---|
| Products Containing ***WEAK ACID (WA)*** Active Ingredients | |
| 2,4-D LV4; *2,4-D* | LANDMASTER BW; *Glyphosate + 2,4-D* |
| **ACHIEVE LIQUID**; *Tralkoxydim* | LANDMASTER II; *Glyphosate + 2,4-D* |
| **AFFINITY BroadSpec**; *Thifensulfuron-methyl + tribenuron-methyl* | **MAVERICK**; *Sulfosulfuron* |
| **AFFINITY TankMix**; *Thifensulfuron-methyl + tribenuron-methyl* | **OUTRIDER**; *Sulfosulfuron* |
| **ALLY Extra SG**; *Thifensulfuron-methyl + tribenuron-methyl + metsulfuron-methyl* | **OLYMPUS 70 WDG**; *Propoxycarbazone-sodium* |
| **ALLY XP**; *Metsulfuron-methyl* | **OLYMPUS FLEX**; *Propoxycarbazone-sodium + mesosulfuron-methyl* |
| **AMBER Custom Pak**; *Triasulfuron* | **ORION**; *Florasulam + MCPA* |
| ASSERT; *Imazamethabenz-methyl* | OSPREY; *Mesosulfuron-methyl* |
| ASSURE II; *Quizalofop-P-ethyl* | PARAMOUNT; *Quinclorac* |
| BANVEL; *Dicamba* | **PEAK**; *Prosulfuron* |
| BEYOND; *Imazamox* | POAST PLUS; *Sethoxydim* |
| BRONATE ADVANCED; *Bromoxynil + MCPA* | POAST; *Sethoxydim* |
| BUCTRIL 4EC; *Bromoxynil* | **POWERFLEX**; *Pyroxsulam* |
| BUCTRIL; *Bromoxynil* | **POWERFLEX HL**; *Pyroxsulam* |
| CLARITY; *Dicamba* | PUMA 1EC; *Fenoxaprop-p* |
| CURTAIL M; *Clopyralid + MCPA* | PURSUIT; *Imazethapyr* |
| CURTAIL; *Clopyralid + 2,4-D* | **RAVE**; *Triasulfuron + dicamba* |
| DISCOVER NG; *Clodinafop-propargyl* | RHONOX; *MCPA* |
| EVEREST 2.0; *Flucarbazone-sodium* | ROUNDUP; *Glyphosate* |
| **EXPRESS**; *Tribenuron-methyl* | SELECT 2 EC; *Clethodim* |
| FALLOW MASTER Broadspectrum; *Glyphosate + dicamba* | SELECT MAX; *Clethodim* |
| **FINESSE Cereal and Fallow**; *Chlorsulfuron + metsulfuron-methyl* | **SHARPEN**; *Saflufenacil* |
| **FINESSE Grass and Broadleaf**; *Chlorsulfuron + flucarbazone-sodium* | SIERRA; *Flucarbazone-sodium* |
| **GLEAN XP**; *Chlorsulfuron* | **STARANE FLEX**; *Florasulam + fluroxypyr* |
| **GOLDSKY**; *Florasulam + pyroxsulam + fluroxypyr* | STINGER; *Clopyralid* |
| **HARMONY Extra SG**; *Thifensulfuron-methyl + tribenuron-methyl* | **SUPREMACY**; *Thifensulfuron-methyl + tribenuron-methyl + fluroxypyr* |
| **HARMONY SG**; *Thifensulfuron-methyl* | THISTROL; *MCPB* |
| **HUSKIE COMPLETE**; *Pyrasulfotole + bromoxynil + thiencarbazone-methyl* | TORDON 22K; *Picloram* |
| **HUSKIE**; *Pyrasulfotole + bromoxynil* | WEEDMASTER; *Dicamba + 2,4-D* |
| | WIDEMATCH; *Clopyralid + fluroxypyr* |
| Products Containing ***NONIONIC POLAR (NP)*** Active Ingredients | |
| AIM EC; Carfentrazone-ethyl | KARMEX DF; Diuron |
| AIM EW; Carfentrazone-ethyl | LOROX DF; Linuron |
| AXIAL STAR; Pinoxaden (also contains a WA, fluroxypyr) | PROWL 3.3 EC; Pendimethalin |
| **AXIAL TBC**; Pinoxaden (also contains a WA, florasulam) | PROWL H20; Pendimethalin |
| EPTAM 20-G; EPTC | SONALAN 10G; Ethalfluralin |
| EPTAM 7-E; EPTC | SONALAN HFP; Ethalfluralin |
| EPTAM 8-E; EPTC | TREFLAN 4L; Trifluralin |
| FAR-GO; Triallate | VALOR SX; Flumioxazin |
| Products Containing ***WEAK BASE (WB)*** Active Ingredients | |
| AXIOM DF; Metribuzin (also contains a NI, flufenacet) | METRIBUZIN 75 DF; Metribuzin |
| Products Containing ***CATIONIC (CA)*** Active Ingredients | |
| GRAMOXONE SL; Paraquat | GRAMOXONE INTEON; Paraquat |
| GRAMOXONE SL 2.0; Paraquat | |

Source: Adapted from The Herbicide Handbook (Shaner 2014).

Table 2. Commonly used Active Ingredients in the Inland PNW-DLR and their Water Solubility(s). Active ingredients are grouped by the charge of the active ingredient and polarity classification, and presented in alphabetical order within classification. The active ingredients where the water solubility changes with pH are bolded and underlined. Note the differences in water solubility values between many of the nonionic polar active ingredients compared to many of the active ingredients in the weak acid, as well as the weak base, and cationic classification. Increased or decreased water solubility is a result of the active ingredient's charge and polarity characteristics. In general, the water solubility determines if the herbicide is more likely to associate with the soil colloids or dissolve into the soil water solution. Higher water solubility results in more herbicide in the soil water solution; the most notable exceptions are paraquat and glyphosate.

| Herbicide charge and polarity classification | | |
|---|---|---|
| **Common Name** | **Chemical Family** | **Water Solubility at 68-77°F (mg/L)** |
| **Weak Acid Active Ingredients** | | |
| 2,4-D | Phenoxycarboxylic acid | 569 (acid); 729,000 (amine); 0.1 (ester) |
| Bromoxynil | Nitrile | 130 (acid); 0.1 (ester) |
| Chlorsulfuron | Sulfonylurea | 587 (pH 5); 31,800 (pH 7) |
| Clethodim | Cyclohexanedione (DIMs) | 0.5 |
| Clodinafop-propargyl | Aryloxyphenoxypropionate (FOPs) | 4.0 |
| Clopyralid | Pyridine carboxylic acid | 1000 (acid); 300,000 (salt) |
| Dicamba | Benzoic acid | 4500 (acid); 720,000 (salt) |
| Fenoxaprop-p | Aryloxyphenoxypropionate (FOPs) | 0.9 |
| **Florasulam** | Triazolopyrimidine | 84 (pH 5); 6360 (pH 7); 94,200 (pH 9) |
| Flucarbazone-sodium | Sulfonylaminocarbonyltriazolinone | 44,000 (pH 4-9) |
| Fluroxypyr | Pyridine carboxylic acid | 4000 (acid); 0.01(ester) |
| **Glyphosate** | Glycine | 15,700 (acid); 900,000 (pH 7) and 786,000 (pH 5) Isopropylamine salt; 4,300,000 (pH 7) Trimethylsulfonium salt |
| Imazamethabenz-methyl | Imidazolinone | 1370 (m-isomer); 857 (p-isomer) |
| Imazamox | Imidazolinone | Miscible |
| Imazethapyr | Imidazolinone | 1400 |
| MCPA | Phenoxycarboxylic acid | 825 (acid); 270,000 (salt); 866,000 (salt); 5 (ester) |
| MCPB | Phenoxycarboxylic acid | acid practically insoluble; 200,000 (salt) |
| Mesosulfuron-methyl | Sulfonylurea | 483 |
| **Metsulfuron-methyl** | Sulfonylurea | 548 (pH 5); 2790 (pH 7); 213,000 (pH 9) |
| Picloram | Pyridine carboxylic acid | 430 (acid); 200,000 (salts) |
| **Propoxycarbazone-sodium** | Sulfonylaminocarbonyltriazolinone | 2900 (pH 4); 42,000 (pH 7-9) |
| **Prosulfuron** | Sulfonylurea | 30 (pH 5.1); 3580 (pH 6.8) |
| **Pyrasulfotole** | Pyrazole | 4200 (pH 4); 69,100 (pH 7); 49,000 (pH 9) |
| **Pyroxsulam** | Triazolopyrimidine | 16.4 (pH 4); 3200 (pH 7); 13,700 (pH 9) |
| Quinclorac | Quinoline carboxylic acid | 62 |
| Quizalofop-P-ethyl | Aryloxyphenoxypropionate (FOPs) | 0.3 |
| **Saflufenacil** | Pyrimidindione | 30 (pH 5); 2100 (pH 7) |
| Sethoxydim | Cyclohexanedione (DIMs) | 120 |
| **Sulfosulfuron** | Sulfonylurea | 17.6 (pH 5); 1627 (pH 7); 482 (pH 9) |
| **Thifensulfuron-methyl** | Sulfonylurea | 223 (pH 5); 2240 (pH 7); 8830 (pH 9) |
| **Tralkoxydim** | Cyclohexanedione (DIMs) | 6 (pH 5); 6.7 (pH 6.5); 8850 (pH 9) |
| **Triasulfuron** | Sulfonylurea | 32 (pH 5); 815 (pH 7); 13,500 (pH 9) |
| **Tribenuron-methyl** | Sulfonylurea | 48 (pH 5); 2040 (pH 7); 18,300 (pH 9) |
| **Nonionic Polar Active Ingredients** | | |
| Carfentrazone-ethyl | Triazolinone | 12,000 (68˚F); 22,000 (77˚F); 23,000 (86˚F) |
| Diuron | Urea | 42 |
| EPTC | Thiocarbamate | 370 |
| Ethalfluralin | Dinitroaniline | 0.3 |
| Flufenacet | Oxyacetamide | 56 |
| Flumioxazin | N-phenylphthalimide | 1.8 |
| Linuron | Urea | 75 |
| Metolachlor | Chloroacetamide | 488 |
| Pendimethalin | Dinitroaniline | 0.3 |
| Pinoxaden | Phenylpyrazoline (DEN) | >200 |
| Pyroxasulfone | Isoxazoline | 3.5 |
| Triallate | Thiocarbamate | 4 |
| Trifluralin | Dinitroaniline | 0.3 |
| **Weak Base Active Ingredients** | | |
| Metribuzin | Triazinone | 1100 |
| **Cationic Active Ingredients** | | |
| Paraquat | Bipyridylium | 620,000 |

Source: Adapted from the Herbicide Handbook (Shaner 2014).

Soil pH can have an influence on the growth of microorganisms in general, and possibly on the growth of microorganisms that degrade herbicides. A medium to high soil pH favors the growth of bacteria populations, whereas a soil with a lower pH (below 4.5) will favor the growth of fungi.

As herbicides are applied, shifts in microorganism populations can occur as the presence of some herbicides can benefit one group of organisms and injure another (Monaco et al. 2002). Once the herbicide is degraded, population densities generally return to ratios present before the herbicide application, while a shift in microbial populations as a result of pH change, would continue to affect microbial populations until neutral pH was restored.

A prolonged change in soil microorganism population, as a result of low or high soil pH, could lead to variation in herbicide persistence based on the microorganism population supported during the period of low or high soil pH.

## Weak Base and Cationic Herbicides

Weak base and cationic herbicides have drastically different activities and persistence in soil. The only weak base active ingredient commonly used in the inland PNW-DLR is metribuzin, and a commonly used cationic active ingredient is paraquat. Metribuzin is the active ingredient found in Metribuzin 75DF (Group 5) and paraquat is the active ingredient found in Gramoxone Inteon (Group 22).

Metribuzin, a weak base, only moderately adsorbs to soil particles and *adsorption* decreases as soil pH increases. In low pH soils, metribuzin becomes cationic and adsorbs to negatively charged soil particles (Figure 1). Thus, the activity of metribuzin decreases with decreasing soil pH because a majority of the herbicide would be positively charged, adsorbed tightly to the negatively charged soil particles, and be unavailable for absorption by plant roots.

As paraquat comes in contact with soil, the cationic (positively charged) herbicide rapidly and tightly adsorbs to the negatively charged soil particles. In fact, paraquat is bound so tightly that it is inactive as an herbicide in the soil. Soil pH has little effect on the activity and persistence of paraquat (Figure 1).

Glyphosate, a weak acid, also binds tightly to soil rendering residues immobile in the soil and unavailable for plant uptake. The binding of glyphosate to soil is a result of a phosphonic acid group in the herbicide structure. The phosphonic acid group (with a net negative charge) binds to cations, such as calcium, iron, or aluminum, which are associated with the negative sites on the soil colloids.

***The water solubility of herbicides is a major factor in determining application timing, rate, formulation, and methods. Therefore, it is extremely important to follow the label.***

## Conclusion

Soil pH in the inland PNW-DLR poses unique challenges for agricultural professionals in the region. The activity and persistence of many inland PNW-DLR herbicides are affected by soil pH. The effects are not always simple, but are often heavily influenced by the unique herbicide structure, and whether or not it has weak acid, weak base, cationic, or nonionic polar properties.

In order to minimize the risk of herbicide injury or carryover to succeeding crops, it is important to know your soil characteristics, including soil pH. Refer to the herbicide label for region-specific guidelines about use rates and rotation restrictions for your soil conditions.

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