

INTERACTION OF SOIL APPLIED HERBICIDES WITH SOIL PH

D.W. Franzen and R.K. Zollinger

Management of soil pH is important in enhancing the availability of certain plant nutrients and in minimizing toxic levels of other elements to crops. However, the reaction of herbicides with soils under varying soil pH levels can affect both crop growth and herbicide performance.

Soil pH affects herbicide performance in several ways. When crops are under stress due to nutrient imbalance from unfavorable soil pH levels, application of certain herbicides may increase risk of crop injury. When soil pH is too high or low, herbicide performance may be unsatisfactory, or persistence of herbicide activity may be lengthened so that crop rotation options are limited. Identification of herbicides affected by soil pH is important in developing crop production programs which not only result in satisfactory weed control, and increase crop safety and flexible crop rotations.

Many crops yield well across a wide range of their adapted pH ranges, the potentially detrimental effects of increased activity of herbicides on initial cropping year yields and on the carryover potential to subsequent crops are perhaps a more important reason why variable pH levels within fields should be mapped, understood and monitored by producers before making herbicide decisions.

Increased susceptibility to herbicide injury because of crop stress caused by nutrient deficiency from high or low pH.

Balancing risk of herbicide injury against the cost of weed control is a dilemma faced by producers annually. In some regions, high pH soil may occur in generally unproductive areas, such as ditchbanks and poorly drained areas (Figure 1). However, in other areas (Figures 2 and 3), high pH soils are usually as productive as the remainder of the field, given that adapted crop varieties are grown. For generally unproductive areas, a producer may choose chemical weed control despite the risk and tolerate injured crops for a week to 10 days until they recover as some labels suggest. When using these herbicides on stressed crops under less than ideal environmental conditions, loss of crop stand has been observed.

The problem is more complex in situations such as shown in Figure 4, where the spatial variability of the high soil pH is at a smaller scale. When crops are already under stress from pH imbalance, choosing herbicides that do not rely on the crops ability to metabolize for selectivity is preferred. Photosynthetic inhibitors and cell membrane disrupters may appear to act more quickly, however, other herbicides with other modes of action may also cause increased chlorosis and metabolic injury. The applicator may also wait until the crop recovers before spraying, although weeds may outgrow their susceptibility to the herbicide during that time. If herbicide choices are limited, the _____

Extension Soil Specialist and Extension Weed Control Specialist, North Dakota State University, Fargo, ND, 58105-5758.

Presented at the North Central Extension-Industry Soil Fertility Conference, November 19-20, 1997, St. Louis, MO.

producer may choose to grow another crop if past experiences with available herbicides were too severe.

Table 1. Common names of herbicides particularly affected by high soil pH levels through increased crop injury when crops are affected by nutrient deficiency symptoms (iron chlorosis). Nearly all other herbicides may also produce increased injury to crops already stressed by excessively high or low soil pH.

| Common name | Trade names | Crop |
|-------------|--|---------|
| Bentazon | Basagran/Storm/Galaxy | Soybean |
| Aciflourfen | Blazer/Storm/Galaxy | Soybean |
| Lactofen | Cobra | Soybean |
| Metribuzin | Sencor/Lexone/Canopy | Soybean |
| Atrazine | Aatrex, Atrazine, Bicep, Laddock, others | Sorghum |

At soil pH levels greater than 7.0, some soybean varieties exhibit degrees of iron chlorosis. Iron is less available to soybeans at high pH levels to soybeans partly because of iron solubility. At high pH, soil may contain high levels of free carbonate minerals such as calcium or magnesium carbonates. Elevated levels of bicarbonates in these soils decrease the soybean ability to solubilize soil iron. Lack of iron decreases the photosynthetic efficiency in leaf tissue. At pH of 8 or above, iron chlorosis affects other crops, such as sorghum and corn.

The herbicides in Table 1 affect photosynthesis. Their application can result in an additive affect on crops already stressed iron chlorosis symptoms. In soybeans, application of Bentazon, Aciflourfen, Lactofen and premixes and tank mixes of these products may result in increased reaction to the herbicide than normally experienced under lower pH conditions. Labels of these herbicides contain precautionary statements concerning unfavorable environmental conditions at application and against applying the herbicides to plants are already stressed from previously applied herbicides. There is no specific precautionary statement on herbicide labels regarding stress from iron chlorosis. Since sorghum is sensitive to atrazine and requires the addition of a softening agent (Concept) seed treatment, incidence of iron chlorosis increases the risk of herbicide injury from atrazine.

Ideally, postemergence herbicides should be applied when crops are not exhibiting symptoms. However, iron chlorosis symptoms are most evident when soybeans are in the one to three leaf stage of growth, which also coincides with the ideal time to control weeds. Herbicide application earlier than recommended may miss some weed germination, while later applications allow larger weeds that may escape control.

Metribuzin, a photosynthetic inhibitor, has greater soil availability and activity in high pH soils. The combination of increased activity and mode of action often results in increased crop injury to soybeans in high pH soils. The metribuzin labels of Sencor and Lexone instruct the user not to apply to soils with pH levels greater than 7.5 or on soils with a calcareous surface layer. There are no pH restrictions given for potato and restrictions on use in alfalfa are for pH levels greater than 8.2 on soil with high levels of

sodium or lime with a calcareous surface west of the Rockies. Sencor used for certain tolerant varieties of barley and winter wheat in a number of western and southern states carries the restriction of use only in soils low in lime, sodium or calcareous surface layers and with a pH less than 7.7.

Herbicides with greater carryover at low pH present a different kind of concern. Separating the effects of herbicide activity with the detrimental effects of low pH, especially with pH levels below 5.0, is difficult. Soil pH below 5.0 may have increased levels of certain nutrient deficiencies and aluminum toxicity, which can impact crop growth and yield. Companies marketing herbicides with greater risk of injury and carryover at low pH internally contend that maintaining pH levels higher than 5.6 is a part of good farm management. However, many fields from the North Central region have areas within fields with pH lower than 5.6. Unfortunately few companies have publicized the problems of carryover or increased activity due to low pH.

High pH soils increase the persistence and carryover potential of some herbicides

Differences in soil pH affect the persistence of certain herbicides due to its affect on microbial activity and a process called hydrolysis (Figure 5). Microbes are sensitive to soil environment much like plants. If pH conditions slow the activity of microbes that work to breakdown herbicides, then herbicide breakdown will decrease. Metribuzin is broken down primarily by microbes, with hydrolysis of little consequence at pH levels between 5-9. Carryover potential is higher at pH levels over 7. Carryover potential may also be increased by decreased adsorption at higher pH levels, with more of the herbicide available for plant uptake at higher pH levels.

A decrease in the rate of hydrolysis is a much more common problem at high pH levels. Hydrolysis of a herbicide in soils is a purely chemical reaction initiated by soil acidity. In the hydrolysis of a chemical ester (R-C-O-C-R, where R is some attached chemical group, C is the esterified carbon and O is oxygen),



When soil pH is not acidic, this reaction does not occur. Depending on the herbicide, hydrolysis proceeds on different areas of the herbicide molecule, but essentially the basic reaction involves cleavage of the molecule at some vulnerable point by water in a pH lower than a critical level. Essentially no hydrolysis occurs at pH >7.

Families of herbicides that rely on hydrolysis for breakdown include the sulfonylureas and some triazines. Sulfonylureas are hydrolyzed between the sulfonyl and urea groups in the molecule. In addition to decreased hydrolysis, solubility of sulfonylurea herbicides greatly increases with increasing pH. Increasing pH from 5 to 7 increases solubility from 548 ppm to 2,790 ppm for Ally, and from 3 ppm to 5,243 ppm for Beacon. Sulfonylurea (SU) herbicides are bound more tightly to soil particles at low pH than at high pH. As soil pH increases, more SU herbicide is negatively charged, which allows less binding to soil and organic matter. In a free form, they are more likely to be available for plant uptake to subsequent crops (Figure 5).

Some sulfonylurea herbicides not listed in Table 2, such as Permit (halosulfuron)

are degraded by both hydrolysis and microbial breakdown. The combination of degradation pathways reduces the possibility of carryover to other crops. Permit is also unique in that hydrolysis occurs at high pH levels. Matrix (rimsulfuron) is also an exception and is broken down by hydrolysis at both pH levels above and below 7.0, with the lowest hydrolysis at pH 7.

Triazine herbicides are more active and persistent in high pH soils. Triazines are generally low in volatility and are not broken down by photodegradation. Hydrolysis is the major mechanism for degradation at pH levels from 5.5 to 6.5. In atrazine, hydrolysis occurs at the 6-chloro group, producing hydroxyatrazine. Cyanazine, which is also a triazine, carryover is not a problem because microbes metabolize a C-N group, neutralizing its phytotoxic activity.

Triazines tend to be positively charged at pH levels less than 7.5, increasing the portion of triazine bound to soil and organic matter. At higher pH, triazines tend to have a neutral charge, decreasing the binding to soil particles and allowing a higher proportion of herbicide to be biologically active.

Table 2. Rotational problems due to carryover at high pH levels.

| <u>Common name</u> | <u>Trade name</u> | <u>Restricted pH levels</u> |
|---------------------------|--------------------------------|---|
| Accent | Nicosulfuron | None for most crops, restriction intervals increase for sorghum at $\text{pH} \geq 7.5$ and sugarbeet at $\text{pH} \geq 6.5$. |
| Atrazine | Atrazine, Aatrex, others | > 7.5 |
| Simazine | Princep 4L, Princep 90DF | > 7.5 |
| Metsulfuron | Ally | > 7.9 |
| Trisulfuron | Amber | > 7.9 |
| Primisulfuron | Beacon | Not specified. Caution to sugarbeet growers in the Red River Valley (pH levels 7.8-8.5 common) |
| Chlorimuron ethyl | Classic, Canopy, Synchrony STS | > 6.8 Canopy > 7.0 Classic |
| Metsulfuron/chlorsulfuron | Finesse | depending on subsequent crop, restrictions range from ≥ 6.5 to ≥ 7.9 |
| Chlorsulfuron | Glean | > 7.9 |
| Prosulfuron | Peak | Depending on subsequent crops, restricted pH ranges from ≥ 7.2 to ≥ 7.8 |
| Prosulfuron/Primisulfuron | Exceed | |

Table 3. Solubility of sulfonylurea herbicides as affected by pH

| Sulfonylurea | ---Solubility (mg/L)----- | |
|------------------|---------------------------|-------------|
| <u>Herbicide</u> | <u>pH 5</u> | <u>pH 7</u> |
| Ally | 548 | 2,790 |
| Amber | 32 | 815 |
| Beacon | 3 | 5,243 |
| Classic | 11 | 5,450 |
| Express | 48 | 2,040 |
| Glean | 587 | 31,800 |
| Peak | 30 | 3,580 |
| Permit | 15 | 1,630 |
| Pinnacle | 223 | 2,240 |

WSSA Herbicide Handbook, 7th edition, 1994.

Several groups of herbicides are broken down primarily at higher pH and risk of carryover to subsequent crops increases as pH levels decrease. The isoxazolidinone family with Clomazone (Command, Commence) as its only member is a unique chemical family where microbial breakdown is the primary degradation pathway. At pH levels at or below 5.9, microbial activity greatly decreases. Problems of carryover increase as the pH decreases.

Imidazolinone herbicides include Assert (Imazamethabenz), Scepter (Imazaquin) and Pursuit (Imazethapyr). Imidazolinone herbicides are not broken down by microbes, are not volatile, are not affected by photodecomposition, nor are they influenced by hydrolysis. Free solubility within the soil solution is important to microbial activity on these compounds. At pH levels at or below 6.5, imidazolinone herbicides have a negative charge, which reduces adsorption onto soil organic matter. For each 0.2-0.4 pH unit decrease, the amount of imidazolinone herbicide adsorbed doubles. When the herbicide is bound, it is not attacked by microorganisms and persists longer in the soil. Other factors contributing to carryover of these compounds include environmental conditions detrimental to microbe activity, such as soil moisture and temperature.

Triazolopyrimidine sulfonanilide herbicides (Broadstrike (flumetsulam), FirstRate) are broken down by soil microbes and are not influenced by volatility, photodecomposition or hydrolysis. Broadstrike is more adsorbed by organic matter and clay at low pH and less adsorbed at high pH. At soil pH >7.0, Broadstrike is less adsorbed and more available for microbial degradation. So for best weed control and least risk of carryover, application to soil with a pH >6.0 is recommended, especially when organic matter levels are greater than 5%. Application at pH levels >7.8 is not recommended because of the risk of crop damage.

Table 5. Rotational problems due to carryover at low pH levels.

| | | |
|-------------|----------------|---|
| Assert | Imazamethabenz | None stated on label, likely levels ~ <6.5 ≤5.9 Scepter and Pursuit labels carry no pH restriction, however, pH levels of 6.5 and less result in greater adsorption and greater risk of carryover potential to subsequent crops. <5.9 and OM>5% |
| Command | Clomazone | |
| Scepter | Imazaquin | |
| Pursuit | Imazethapyr | |
| Broadstrike | Flumetsulam | |

Injury symptoms from pH interactive herbicides

Photosynthetic injury on crops comes from interruption of the food producing process in susceptible plants by binding to specific sites within the plants chlorophyll system. Injury symptoms from this type of injury are believed to come not from slow starvation, but from the formation of toxic secondary products within the plant. Cotyledons are not affected, and symptoms will first be seen on true leaves. Symptoms include yellowing of the leaf tissue first at the leaf margins and tips. In broadleaf plants, interveinal leaf injury will be observed. Older, more mature leaves will be first affected. If the injury is severe, the symptoms may spread to all leaf tissue. the leaves will become necrotic and die.

Injury from Clomazone (Command, Commence) comes from the plants inability to produce pigments. Plant leaves will appear pale yellow or white. Newly developed leaves are most susceptible to injury.

Imidazolinone and sulfonylurea injury is observed as stunting of grassy crops, with interveinal yellowing (chlorosis) or purpling. Corn plants are stunted and may have a "spiked" appearance caused by problems with slow leaf unfurling. Plant roots are stunted with lateral roots poorly developed. Soybean, sugarbeet, sunflower, canola and other broadleaf crops will show stunting to death of the terminal bud. Leaves may be yellow and leaf vein colors may range from purple to red.

Meeting the challenges of pH sensitive herbicides

It will take a combination of producer education, soil sampling and mapping activity to more accurately describe soil pH levels in individual fields, and industry involvement in better publication of pH restrictions in order to find practical solutions to the problem of pH sensitive herbicides.

Some companies have gone to great lengths in their labels to spell out pH restrictions for subsequent crops, while others seem to rely on local sales representatives to provide carryover and crop restriction information. Other companies may have limited knowledge of product performance under pH extremes, or the information may have been omitted by marketing personnel to improve the product image. Several products have been registered without reliable data on herbicide data on herbicide breakdown and degradation. Consequently, producers and ag-retailers find two years later that local conditions of high/low pH produced areas of excessive crop damage and distrust due to

carryover. Having good data in hand before product registration would help make product introduction of pH sensitive herbicides less painful for end-users and retailers. Making technical publications readily available to producers explaining the affects of pH on herbicide effectiveness and persistence would be valuable to ag-supply stores and the producers and help prevent unfortunate situations.

In many areas, past use of certain photosynthetic herbicides for corn and soybeans have made many producers aware of areas within fields with high pH problems, but the new herbicides with low pH carryover concerns are breaking new ground. Only dense gridding, or sampling in some logical manner based on field history will give enough information to help map high and low pH areas. Fortunately, analysis for soil pH is relatively inexpensive. To define areas of high or low pH, perhaps even portable test kits can be utilized which can be then checked with an approved laboratory for verification of certain areas in between critical levels.

In no-till and minimum tillage fields, the traditional method of 0-6 inch or 0-8 inch soil cores may not be adequate. Instead, a 0-2 inch core depth and a 2-6 inch core depth may be needed, since application of limestone to the surface may increase surface pH more than expected or application of nitrogen fertilizer to the surface may cause a drop in pH at the surface. Both conditions could affect herbicide performance and carryover potential.

Managing pH sensitive herbicides and crop rotations requires information, communication and good decision making. Information about the pH sensitivity and restrictions comes from the manufacturer and developer. Information about local pH levels at a relevant spatial scale comes from the producer and ag-supply dealer. Good communication is needed between all parties, and finally the decision is made concerning whether the product is a good choice for the farm or whether it would be best to select another option. If the pH problem can be prevented by limestone application to raise soil pH, then the producer should be willing to apply the correct rate of limestone. Lowering pH levels in parts of the field will hardly ever be practical, given the free lime in many of these soils and the cost of amending them.

REFERENCES

Ahrens, W.H., ed. 1994. *Herbicide Handbook*. 7th Edition. Weed Sci. Soc. Am. Champaign, IL.

Chemical and Pharmaceutical Press, Inc. 1996. *Crop Protection Reference*, 12th Edition. New York, NY.

Shaner, D.L. and S.L. O'Connor. 1991. *The Imidazolinone Herbicides*. CRC Press, Boca Raton, FL.

Figure 1. Possible sources of high pH in an east-central Illinois field.

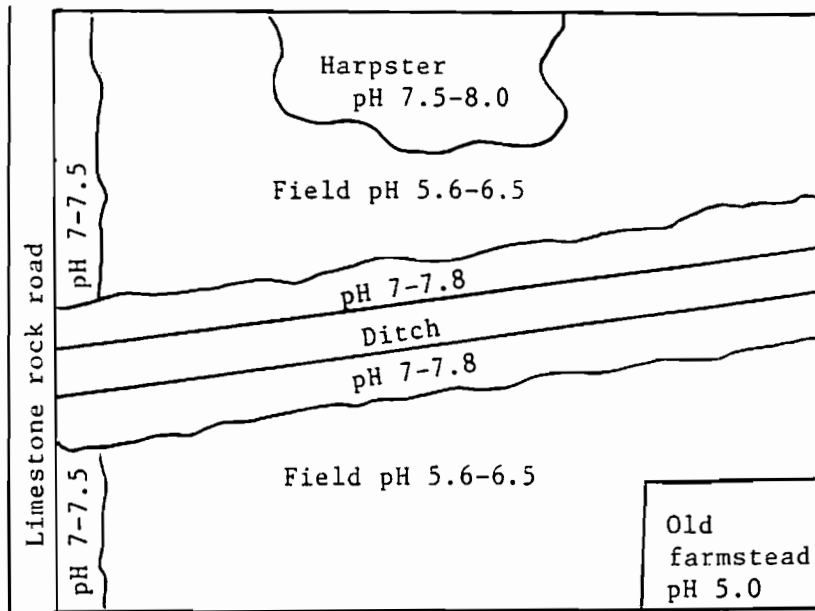
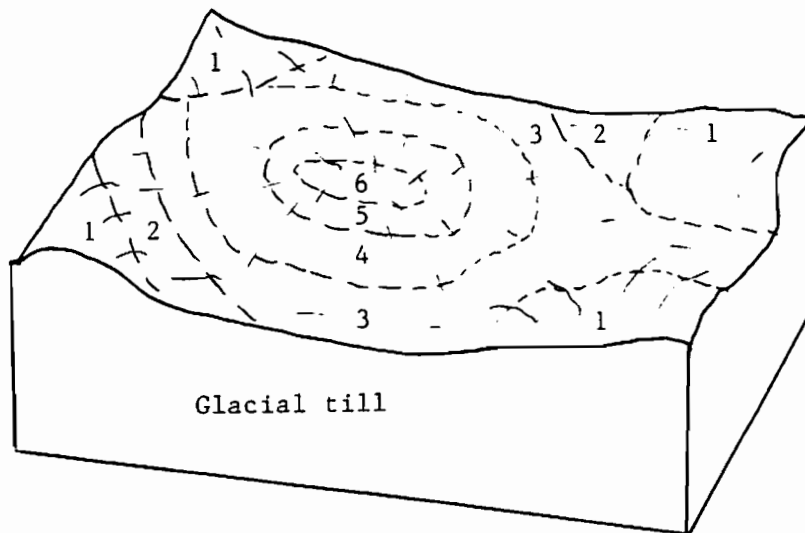
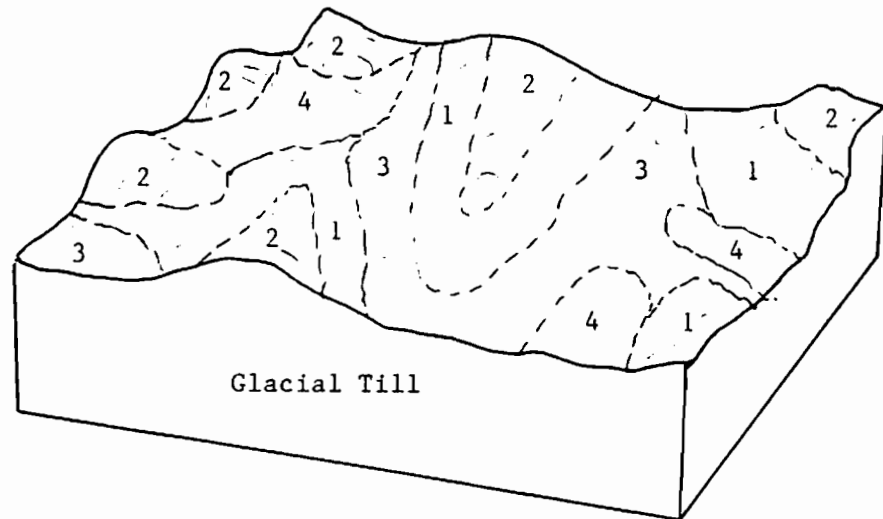


Figure 2. Patterns of soils in an Iowa Clarion-Webster-Canisteo association showing the areas of probable high pH.



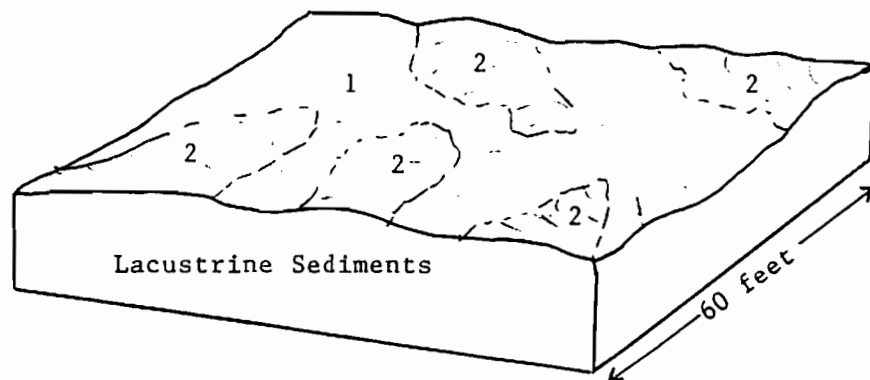
- | | |
|-------------|----------------------------------|
| 1. Clarion | 4. Canisteo (Calcareous Surface) |
| 2. Nicollet | 5. Harps (Calcareous Surface) |
| 3. Webster | 6. Okoboji (Calcareous Surface) |

Figure 3. Pattern of soils in the glacial till plain of North Dakota, showing areas of high pH and calcareous soils.



1. Barnes (surface carbonates none to slight)
2. Buse (surface carbonates slight to moderate)
3. Svea (surface carbonates none to slight)
4. Hamerly (calcareous surface)

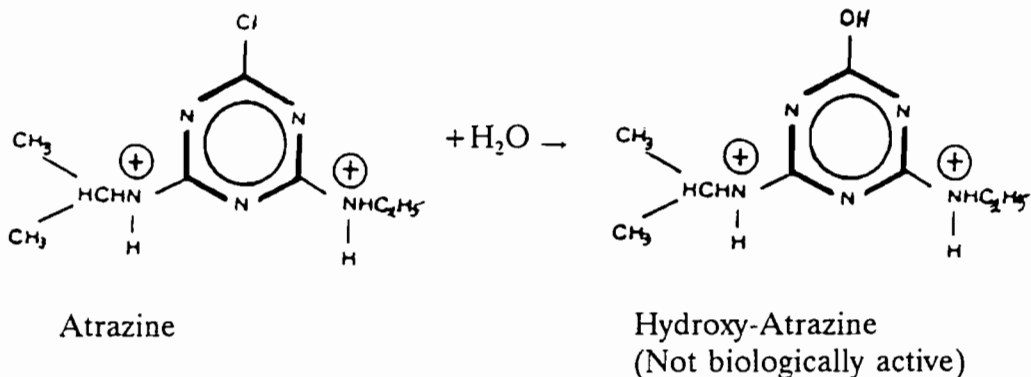
Figure 4. Patterns of soil in the Red River Valley showing the small spatial scale of calcareous soils development in these lacustrine parent materials.



1. Fargo (surface carbonates none to slight)
2. Hegne (calcareous surface)

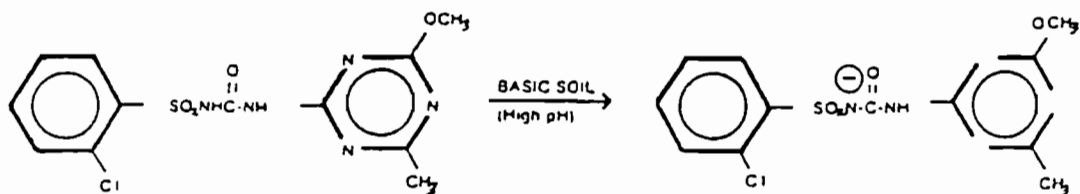
Figure 5. Reaction of certain herbicides to soil pH.

Atrazine hydrolysis at low pH (<7.5).



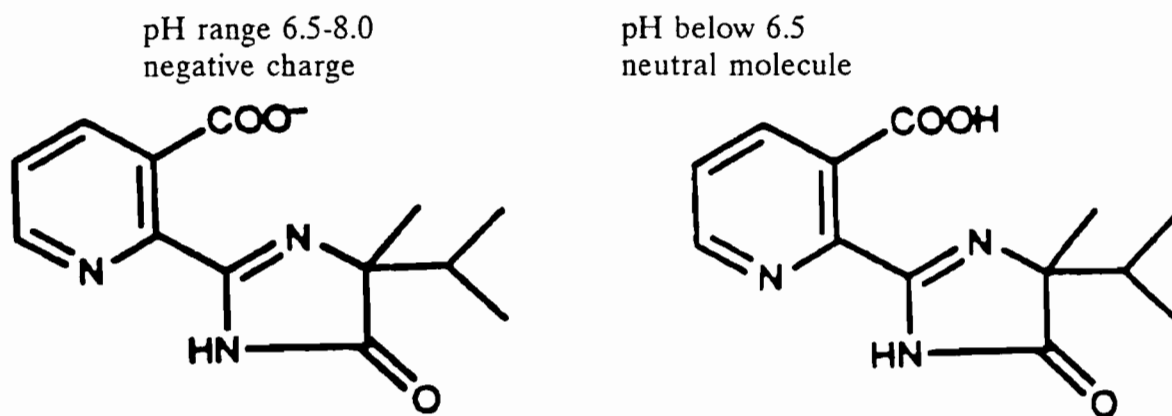
Atrazine hydrolysis is very slow at higher pH.

Glean (Chlorsulfuron) receives a negative charge at high pH.



The negatively charged molecule is not adsorbed by clay or organic matter, also hydrolysis does not occur at high pH to break down the compound.

Imidazolinone reactions to pH differences.



The adsorbed neutral molecules are not available for microbial degradation, therefore carryover potential to sensitive crops increases at low pH.

**PROCEEDINGS OF THE TWENTY-SEVENTH
NORTH CENTRAL EXTENSION-INDUSTRY
SOIL FERTILITY CONFERENCE**

Published for
The North Central Extension-Industry Soil Fertility Conference
by
Potash & Phosphate Institute
772 - 22nd Avenue, South
Brookings, SD 57006
605-692-6280

November 19-20, 1997

St. Louis Westport Holiday Inn
St. Louis, Missouri

Volume 13

Program Chairman and Editor:

Dr. Gary Hergert
University of Nebraska-Lincoln
Institute of Agriculture and Natural Resources
West Central Research & Extension Center
Route 4, Box 46A
North Platte, NE 69101